Corrosion

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TECHNICAL SECTION

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NACE NEWS

15th Conference Report

TECHNICAL TOPICS

THIS MONTH'S COVER—Cold coating being applied to Trans-Canada's 30-inch mainline was formulated for pipe temperature to 275 F. Pipe temperatures are expected to range from 200 F at compressor station discharge to 135 F four miles away. Photograph from Royston Laboratories, Inc., Pittsburgh, Pa.

GENERAL NEWS

Technical Topics Scheduled for June

Five Case Histories on Corrosion Problems in Nitric Acid and Ammonium Nitrate Production and Storage, by D. M. Carr
Solving Corrosion Problems at Electrical Generating Plants, by L. Baskette
Corrosion Keeps Knife Sharp on Fruit Canning Machine, by S. H. Creed
Methods of Testing Characteristics of Polyethylene Jackets for Steel Pipe, by H. M. McDaniel

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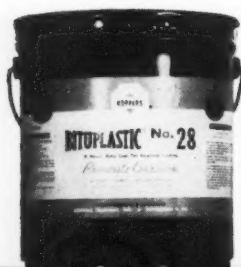
Bituplastic No. 28—almost equal in body to No. 50, and an excellent weather-resistant coating.
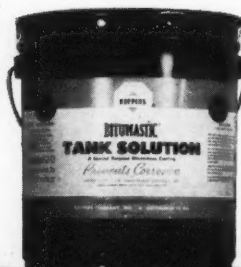
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SCHEDULED FOR PUBLICATION IN JUNE CORROSION

Evaluation of Some Organic Corrosion Inhibitors for Special Application in Petroleum Refining, by R. B. Thompson, R. F. Stedman, Charles Wankat and R. C. Henry

Reprint—Corrosion of Reinforcing Steel in Concrete in Marine Atmospheres, by D. A. Lewis and W. J. Copenhagen

Impedance Characteristics of Isolated Aluminum Oxide Films, by D. F. MacLennan

Analytical Procedure for Testing the Effectiveness of Hydrogen Sulfide Corrosion Inhibitors, by Donald W. Shannon and James E. Boggs

Rates of Dissolution and the Passivation of Hafnium-Free Zirconium in Hydrofluoric Acid, by M. E. Straumanis, W. J. James and A. S. Neiman

Evaluation of Protective Coatings for Ship Bottoms, by J. R. Brown

A Study of the Corrosion of Steel by Oil-Brine H₂S Mixtures, by D. W. Shannon and James E. Boggs

Progress Report on Inhibiting the Corrosion of Steel in a Reinforced Concrete Bridge, by R. F. Stratful

Wash Primers, by L. R. Whiting
Performance of Organic Coatings in Tropical Environments, by A. L. Alexander, B. W. Forgeson and C. R. Southwell

Corrosion

Part 2—Laboratory Investigation

The Effect of Sigma Phase vs Chromium Carbides On the Intergranular Corrosion Of Type 316 and 316L Stainless Steel*

By DONALD WARREN*

Outline of Investigation

THE PURPOSE of this investigation was to study the manner in which chromium carbides and sigma phase affect the intergranular corrosion resistance of Types 316 and 316L stainless steel. Since these alloys are subject to both carbide precipitation and sigma phase formation, the initial problem was to separate the effects of these two phases. This separation was accomplished by using a Type 316 stainless steel heat for the study of carbide precipitation and several Type 316L heats for the study of sigma phase formation. The carbon content (0.05 percent) of the Type 316 heat made it possible to produce a continuous grain-boundary network of chromium carbides by heat-treatment for 2 hours at 1250 F. The lower carbon content (0.025 percent or less) of the Type 316L heats made them relatively free of carbide precipitation after the short-time heat-treatments that were used and, at the same time, increased their tendency to form sigma phase.

In this study, the effect of sigma phase on the corrosion resistance of Type 316L stainless steel was evaluated for three different forms of this phase: (1) a continuous grain boundary network, (2) agglomerated as separate discrete particles in the grain boundaries and (3) partially transformed ferrite in weld metal.

The intergranular corrosion behavior of the Type 316 and Type 316L heats was first evaluated by means of standard laboratory tests. The tests used were the boiling 65 percent nitric acid test, the 10

percent nitric-3 percent hydrofluoric acid test and the electrolytic oxalic acid etching test. Next, the intergranular corrosion behavior of the same heats of steel was studied in those acid media for which these steels are generally used. Many of the latter media were chosen because they had been reported as having intergranularly attacked sensitized stainless steel. The progress of corrosion in the test solution was followed by weight-loss measurements, visual-plus-microscopic examination and progressive photomicrographs of the corroded areas. Finally, the results of the corrosion tests in various acid media were correlated with the data obtained from the standard laboratory tests for susceptibility to intergranular corrosion.

Experimental Details

Types of steel and their heat-treatment

The chemical compositions of the Type 316 and 316L heats used in this study are listed in Table 1. Table 2 gives the heat-treatments employed and the corresponding microstructures. Reference is made in Table 2 to the figures which illustrate the basic microstructures.

Note that chromium carbides were studied only in the form of a continuous grain-boundary network (see Figure 1). Sigma phase was studied in the form of a continuous grain boundary network (1 hour at 1300 F, water quenched) and in the form of separate, discrete particles in the grain boundaries (4 hours at 1600 F, water quenched[1] + 1 hour at 1300 F, water quenched). (See Figure 2.) In heat FI9A, the sigma phase formed rapidly and produced visible etching effects after heat-treatment for 1 hour at 1300 F, water quenched. (See Figure 2B.) In heats FI2A

Abstract

A laboratory study was made of the intergranular corrosion behavior of Types 316 and 316L stainless steel in 14 different acid environments. Included were nitric, nitric-hydrofluoric, acetic, citric, sulfuric, lactic, oxalic, formic and phosphoric acids. Results of this study showed that sensitized or welded Type 316L had excellent resistance to intergranular attack in all of the acid media except nitric. This was true despite the presence of a continuous network of sigma phase in the grain boundaries of the sensitized steel. In contrast, Type 316 having a continuous grain boundary network of chromium carbides underwent severe intergranular corrosion in 12 of the 14 environments studied.   3.2.2

and FI4A, the sigma phase formed so slowly that there was no microscopic evidence of any grain-boundary phase after sensitizing for 1 hour at 1300 F, water quenched. (See Figure 3.)

The presence of sigma phase in these two heats was based on the following indirect evidence: (a) X-ray diffraction data on residues isolated from heats FI2A and FI4A after heat-treatment for 1000 hours at 1300 F showed that sigma phase was definitely formed at 1300 F and (b) the severe intergranular corrosion of heats FI2A and FI4A in the nitric acid test after heat-treatment for 1 hour at 1300 F, water quenched, indicated a grain-boundary phase change of a rather continuous nature.

Sigma phase was also believed to be present in the weld metal of the tungsten inert-arc welded specimens of heats FI9A, FI2A, and FI4A (see Table 2 for welding conditions). In these cases, the presence of sigma phase was based on the severe nitric acid attack on the weld metal rather than on metallographic or X-ray evidence.

Sample preparation

The size of the corrosion specimen was approximately 3/4 by 1 inch. Specimens were heat-treated in a combustion-type

[1] The heat-treatment for 4 hr. at 1600 F is responsible for the agglomeration of sigma phase into separate discrete particles.
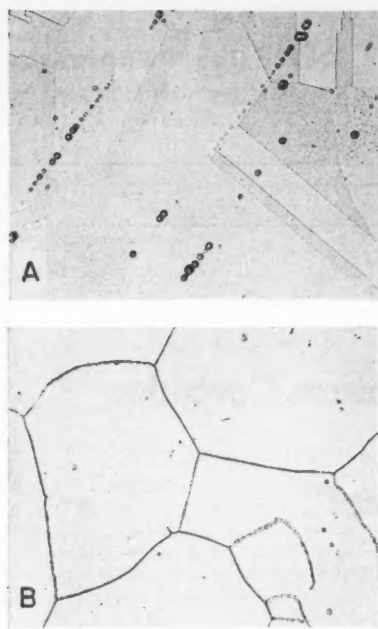
Figure 1—Microstructures of heat MY316 of Type 316 stainless steel at 1000X.

(A)—Commercially annealed; Microstructure: annealed.

(B)—Sensitized 2 hours at 1250 F, water quenched. Microstructure: continuous grain boundary network of chromium carbides.

tube furnace with the temperature controlled within ±10 F.

The tungsten inert-arc welded samples were prepared by making a single pass in the longitudinal direction on strips of plate 1 inch wide by 6 inches long. Smaller specimens about ¾-inch long were then cut from the welded strips. The welds were made at the highest heat input possible without producing burn-through or hot-cracking.

All corrosion specimens were given an 80-grit surface finish by belt-grinding. Also, a ¼-inch square area was electropolished on one of the flat faces of all but the welded specimens. A cross was inscribed on the electropolished square with the diamond indenter of a microhardness tester. The cross-hatched square made it possible to record the progress of corrosion by taking successive photomicrographs of the same area.

Corrosive environments and testing procedure

Standard Laboratory Tests: The boiling 65 percent nitric acid test was made according to the standard ASTM procedure.[1] All but the welded specimens were flask-tested for five 48-hour periods. The welded specimens were tested in a multisample tester[3] for three periods totaling 230 hours.

The 10 percent nitric-3 percent hydrofluoric acid test consisted of five ½-hour periods at a solution temperature of 80 ± 2 C. Fresh solution was used for each test period. Tests were conducted in polyethylene bottles in a constant-temperature water bath.

The electrolytic oxalic acid etching test was made according to standard ASTM procedure.[3] Specimens were electro-
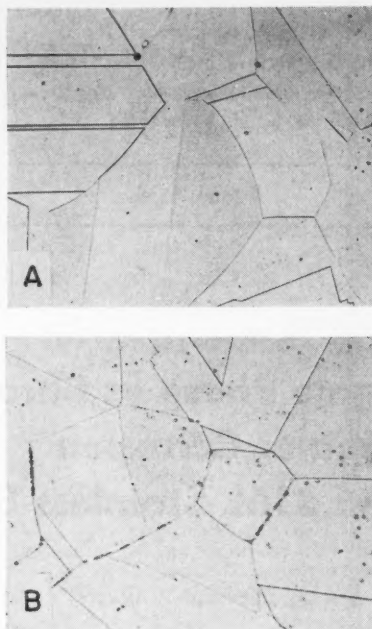
Figure 2—Microstructures of heat F19A of Type 316L stainless steel at 1000X.

(A)—Commercially annealed; Microstructure: annealed.

(B)—Sensitized 1 hour at 1300 F, water quenched. Microstructure: continuous grain boundary network of sigma phase.

(C)—Stabilized 4 hours at 1600 F, water quenched and sensitized 1 hour at 1300 F, water quenched. Microstructure: separate, discrete particles of sigma phase in grain boundaries.

lytically etched in a 10 percent oxalic acid solution for 1.5 minutes at current density of 1 amp/sq cm.

Other Laboratory Corrosion Tests

Test Environments. Table 3 lists the 12 corrosive environments used to evaluate the relative effects of chromium carbides and sigma phase on the intergranular corrosion behavior. These environments, which include seven different organic and mineral acids, were chosen for two reasons. First, with one or two exceptions, they are typical of the service media for which Types 316 and 316L stainless steel are generally used.[4] Secondly, many of these acid media were reported as having caused intergranular corrosion of sensitized stainless steels in service (see Table 1 in Part 1 of this article[2]). The test environment consisting of 30 percent sulfuric acid at

(2)*Corrosion*, 15, 213t (1959) Apr.
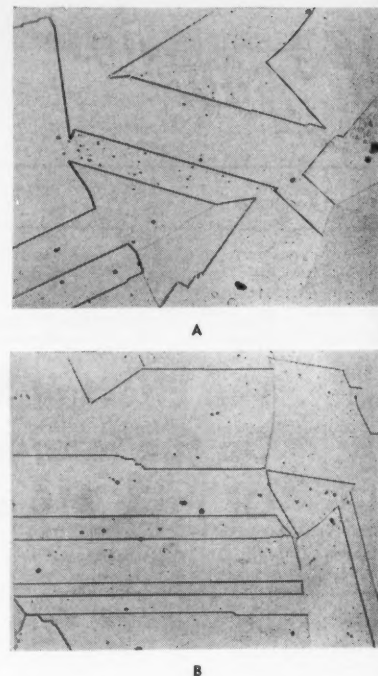
Figure 3—Microstructures of Heats F14A and F12A of Type 316L stainless steel at 1000X.

(A)—F14A: sensitized 1 hour at 1300 F, water quenched. Microstructure: continuous grain boundary network of sigma phase (microscopically invisible but presence of sigma phase based on X-ray diffraction data and on high nitric acid corrosion rates).

(B)—F12A: sensitized 1 hour at 1300 F, water quenched. Microstructure: continuous grain boundary network of sigma phase (microscopically invisible but presence of sigma phase based on X-ray diffraction data and on high nitric acid corrosion rates).

35 C was selected because it was the only environment (other than nitric acid) in which sigma phase was known to seriously decrease the corrosion resistance.[5, 6]

Testing Procedures. Activation of Samples: All corrosion specimens tested in the acid media listed in Table 3 were activated prior to each test period to provide consistent and reproducible results. In the two nonboiling tests, the corrosion specimens were activated electrolytically by the cathodic liberation of hydrogen for 10 to 15 seconds. The activation consisted of applying a small 2 to 3 volt emf across an electrolytic cell of which the corrosion specimen was the cathode, the test solution was the electrolyte and a stainless steel wire was the anode.

In the boiling tests, the corrosion specimens were activated by immersion in a 150 F solution of 15 percent HCl by volume (5.4 percent by weight) until hydrogen was evolved from most of the specimen surface.[7] (This usually required no more than 30 seconds.) After activation, the specimens were rinsed in two flasks of distilled water and then in a boiling solution of the same composition as the test solution. The rinsing was done rapidly to minimize surface-drying before the specimen was immersed in the test solution. This method of activation was used because the weight losses it produced were low (a maximum of 1 mg and in most cases less than 0.4 mg) and the hy-

drochloric acid treatment did not intergranularly attack any of the specimens.

Length of Test Period: The optimum length of test period was individually determined for each test; it varied from 1 to 24 hours. All tests were conducted initially for periods of 30 minutes to 1 hour. The length of the test period was then increased to an optimum from the standpoint of maintaining a uniform corrosion rate while holding the solution contamination to a minimum. In some cases (boiling 10 percent and 45 percent formic acid), long test periods were not practical because semi-protective films of corrosion products rapidly covered the specimens and sharply reduced the rate of attack. In other cases (boiling 10 percent sulfuric acid and 70 percent phosphoric acid), short test periods (1 to 4 hours) were required because high corrosion rates caused rapid contamination of the test solution with corrosion products. Except where otherwise noted, fresh solution was used for each test period.

The total length of each test depended upon both the pattern and the degree of the corrosive attack. When either the general or intergranular corrosion was severe, the total testing time was short. Where the corrosive attack was primarily intergranular but not very rapid, the total testing time was extended to 500 to 1000 hours.

Cleaning of Samples: The corrosion specimens were cleaned at the end of each test period with water and liquid soap to remove any nonadherent films of corrosion product. In the boiling 10 percent oxalic acid test, some of the specimens were heavily coated with oxalate corrosion products. The oxalate coatings were removed by cleaning the specimens in a solution of 15 percent HCl (by volume) at 150 F (weight losses due to the HCl cleaning treatment were insignificant compared to those due to the oxalic acid corrosion).

Field Exposure Test. Corrosion specimens from two heats (FI9A and FI4A) of Type 316L stainless steel were exposed

in the field to a 30 percent nitric-14 percent adipic acid solution at 110 C for seven months. These specimens were exposed in the same conditions of heat-treatment as those used for the laboratory test specimens. (See Table 2.)

Discussion of Results

Standard laboratory tests for susceptibility to intergranular corrosion.

Type 316 Stainless Steel (Effect of Chromium Carbides). The boiling 65 percent nitric acid test, the 10 percent nitric-3 percent hydrofluoric acid test and the electrolytic oxalic acid etching test gave

Figure 4—Corrosion of Type 316 stainless steel (Heat MY316) in boiling 65 percent nitric acid.
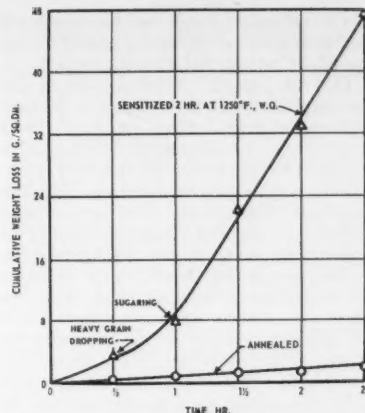
Figure 5—Corrosion of Type 316 stainless steel (Heat MY316) in 10 percent nitric-3 percent hydrofluoric acid at 80 C.

comparable results when applied to the Type 316 stainless steel heat MY316. Each of the three tests indicated a susceptibility to severe intergranular attack when a continuous network of chromium carbides was present in the steel due to sensitizing (2 hours at 1250 F, water quenched).

The sensitized samples of heat MY316 underwent severe intergranular corrosion and grain-dropping in both the nitric acid test and the nitric-hydrofluoric acid test. Figures 4 and 5 show graphically the corrosion behavior of heat MY316 in the two tests. In each figure the increasing slope

TABLE 1—Chemical Composition of Stainless Steel Heats Used for Corrosion Tests

Heat Number*	Type of Stainless Steel	Plate Thickness, Inches	Chemical Composition, Percentage						
			C	Cr	Ni	Mo	Mn	Si	N
MY316....	316	0.25	0.046	17.39	12.70	2.42	1.68	0.61	....
FI2A......	316L	0.27	0.022	17.33	12.91	2.28	0.90	0.36	0.031
FI4A......	316L	0.20	0.020	16.16	13.22	2.20	1.60	0.47	0.029
FI9A......	316L	0.21	0.018	18.54	12.84	3.00	0.71	0.27	0.027

* All of these steels were commercially produced.

TABLE 2—List of Stainless Steels Used for Corrosion Tests and Their Condition of Heat-Treatment

Classification of Stainless Steel	Lab. Heat Number	Condition of Heat-Treatment		Microstructure	Shown in Figure
		Code	Description	Description	
Type 316 heat used for carbide precipitation	MY316	1	Commercially annealed	Annealed	1A
		2	2 hr. 1250°F., W.Q.	Continuous grain boundary network of chromium carbides.	1B
Type 316L heat which was capable of rapid formation of sigma phase	FI9A	1	Commercially annealed	Annealed	2A
		2	1 hr. 1300°F., W.Q.	Continuous grain boundary network of sigma phase which produces visible etching effects.	2B
		3	4 hr. 1600°F., W.Q. + 1 hr. 1300°F., W.Q.	Separate, discrete particles of agglomerated sigma in the grain boundaries.	2C
		4	Tungsten inert-arc welded. (100 amp - 6 in/min)	Base plate: annealed Weld metal: austenite + 6% ferrite	
Type 316L heats which were capable of very slow formation of sigma phase	FI4A and FI2A	1	Commercially annealed	Annealed	
		2	1 hr. 1300°F., W.Q.	Continuous grain boundary network of sigma phase which is microscopically invisible (no visible etching effects)*	3
		4	Tungsten inert-arc welded FI4A (100 amp.- 9 in./min.) FI2A (115 amp.- 6 in./min.)	Base plate: annealed Weld metal: FI4A - completely austenitic FI2A - austenite + 1% ferrite	

* X-ray diffraction data on residues isolated from these heats after 1000 hours at 1300 F have shown that sigma is formed at 1300 F although very slowly. Presence of sigma, or a phase similar to sigma, after only 1 hour at 1300 F is based on high rate of intergranular corrosion of these heats in nitric acid test.

of the corrosion curve for the sensitized specimen reflects the rapid grain-dropping caused by severe intergranular attack.

The ratio of the corrosion rate of the steel in the sensitized condition to the rate in the annealed condition provides a good measure of the degree of intergranular corrosion on the sensitized sample. For example, a ratio of one indicates that the sensitized specimen corroded at the same rate as the annealed specimen and that no appreciable intergranular attack occurred. In the case of heat MY316 this ratio was 109 in the nitric acid test and 22 in the nitric-hydrofluoric acid test. (See Table 4.) The lower ratio in the nitric-hydrofluoric acid test is due probably to the much higher rate of general attack in this solution: 0.31 in./mo. compared to 0.00089 in./mo. for the nitric acid test.

The electrolytic oxalic etch structures correlated well with the results of the nitric acid and nitric-hydrofluoric acid tests. In the annealed condition, heat MY316 had a step structure, indicating freedom from carbide precipitation. (See

TABLE 3—List of Corrosive Environments Used for Laboratory Tests (Excluding Standard Tests)

Solution and Concentration	Test Temperature, C
20% Acetic Acid	102*
20% Citric Acid	102*
Formic Acid 10%	101*
45%	103*
85% Lactic Acid	118*
10% Oxalic Acid	101*
Phosphoric Acid 50%	109*
70%	124*
Sulfuric Acid 0.5%	50
0.5%	101*
10%	101*
30%	35

* Boiling Tests

Figure 6A.) Correspondingly, the annealed specimens of heat MY316 were not intergranularly attacked in either of the two corrosion tests. In the sensitized condition (2 hours at 1250 F, water quenched), heat MY316 had a ditch structure, with 90 percent of the grains encircled by carbides. (See Figure 6B.) This damaging carbide precipitation resulted in severe intergranular corrosion of the sensitized specimens of heat MY316 in both of the corrosion tests.

Type 316L Stainless Steel (Effect of Sigma Phase). The boiling 65 percent nitric acid test, the 10 percent nitric-3 percent hydrofluoric acid test and the electrolytic oxalic acid etching test gave conflicting results when used to evaluate three heats of Type 316L stainless steel: FI9A, FI4A, and FI2A. The principal disagreement was that the nitric acid test was the only one of the three tests which was affected detrimentally by a continuous grain-boundary network of sigma phase.

Effect of Continuous Grain-Boundary Network of Sigma Phase. Those samples of the three Type 316L heats containing a continuous grain-boundary network of sigma phase (produced by sensitizing 1 hour at 1300 F, water quenched) behaved as follows: severe intergranular corrosion and grain-dropping in the boiling 65 percent nitric acid test and no intergranular attack or grain-dropping in the nitric-hydrofluoric acid test. Ratios of the sensitized corrosion rate to the annealed corrosion rate varied from 30 to 130 in the nitric acid test and were approximately one (0.9 to 1.1) in the nitric-hydrofluoric acid test. (see Table 4.) Figure 7 compares the corrosion behavior of heat FI9A of Type 316L stainless steel in the two corrosion tests. Note that in the nitric acid test the sensitized specimen corroded at an accelerated rate due to intergranular attack; whereas in the nitric-hydrofluoric acid test, the sensitized specimen corroded
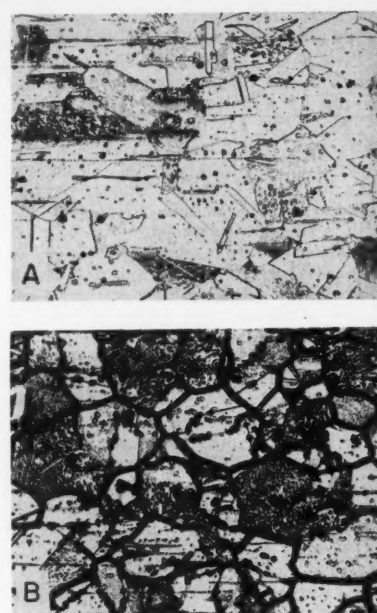
Figure 6—Etch structures for Heat MY316 of Type 316 stainless steel produced by the electrolytic oxalic acid etching test, 250X.

(A)—Commercially annealed; step structure.

(B)—Sensitized 2 hours at 1250 F, water quenched. Ditch structure (90 percent of grains encircled.)

at a linear rate identical with that of the annealed specimen.

The electrolytic oxalic acid etch structures for Type 316L stainless steel sensitized 1 hour at 1300 F, water quenched, were either step or mild dual in nature. When the continuous grain-boundary network of sigma phase produced microscopically visible etching effects (see Figure 2B for heat FI9A), the oxalic acid etch structure was mild dual (see Figure 8B). When the continuous network of sigma phase produced no microscopically visible etch-

TABLE 4—Relative Effects of Chromium Carbides and Sigma Phase on Standard Laboratory Tests for Susceptibility to Intergranular Corrosion

Type of Steel	Lab. Heat No.	Heat-Treatment Code[1]	Microstructure Intergranular Phase That is Predominantly Present	Shown in Figure	Boiling 65% Nitric Acid Test[2] Rate Inches/Month	Ratio[5]	10% Nitric-3% Hydrofluoric acid at 80C[3] Rate Inches/Month	Ratio[5]	Oxalic Acid Etch Test[4] Classification of Etch Structure	Shown in Figure
316	MY316	1	None (Annealed structure)	1A	0.00089		0.31		Step	6A
		2	Continuous network of chromium carbides	1B	0.097 (I)*	109	6.9 (I)*	22	Ditch (90% of grains encircled)	6B
316L	FI9A	1	None (annealed structure)	2A	0.00059		0.20		Step	8A
		2	Continuous network of fine sigma	2B	0.080 (I)	136	0.20	1	Dual (Mild)	8B
		3	Agglomerated sigma (separate, discrete particles)	2C	0.00066	1.1	0.27[6]	1.3	Ditch (Relatively shallow ditching)	8C
316L	FI4A	1	None (Annealed structure)				0.00116		0.72	Step
		2	Microscopically invisible sigma[7]	3A	0.035 (I)	36	0.63	0.9	Step	9A
316L	FI2A	1	None (Annealed structure)		0.00077		0.51		Step	
		2	Microscopically invisible sigma[7]	3B	0.024 (I)	31	0.56	1.1	Step	9B

[1] Heat-treatment code is same as that used in Table 2.
[2] Five 48-hr periods.
[3] Five ½ hr periods.
[4] Electrolytically etched in 10% oxalic for 1.5 min. at a current density of 1 amp/sq cm.
[5] Ratio of corrosion rate for sample containing grain boundary phase to that of corrosion rate for annealed sample (individually calculated for each heat).
[6] Heavy intergranular etching occurred.
[7] This statement based on X-ray diffraction data. See footnote on Table 2.
* (I) denotes severe intergranular attack with heavy grain dropping.
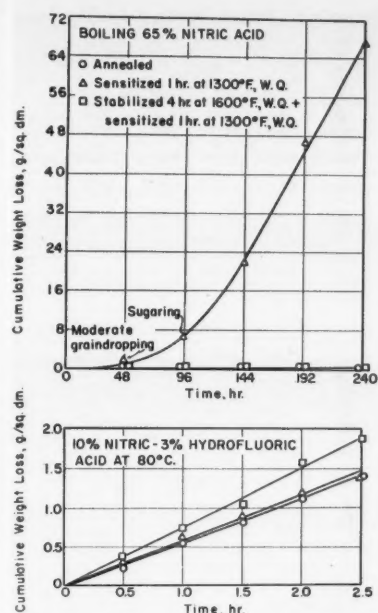
Figure 7—Corrosion of Type 316L stainless steel (Heat FI9A) in boiling 65 percent nitric acid and in 10 percent nitric–3 percent hydrofluoric acid at 80 C.

Figure 9—Etch structures for Heats FI4A and FI2A of Type 316L stainless steel produced by the electrolytic oxalic acid etching test, 250X.

(A)—FI4A: Sensitized 1 hour at 1300 F, water quenched; step structure.

(B)—FI2A: Sensitized 1 hour at 1300 F, water quenched; step structure.

ing effects (see Figures 3A and 3B for heats FI4A and FI2A), the oxalic acid etch structure was step (see Figures 9A and 9B). Neither the step nor mild dual structures obtained are compatible with the high nitric acid corrosion rates of the sensitized specimens of Type 316L stainless steel. However, these oxalic acid etch structures are in agreement with the results of the nitric-hydrofluoric acid test: the absence of damaging carbide precipitation in the oxalic acid etching test (step or mild dual structure) agrees with the freedom from intergranular corrosion in the nitric-hydrofluoric acid test.

Effect of Agglomerated Sigma Phase in the Grain Boundaries. Agglomerated sigma phase in the form of separate discrete particles in the grain boundaries had little or no effect on the corrosion resistance of Type 316L stainless steel in either the boiling 65 percent nitric acid test or in the 10 percent nitric-3 percent hydrofluoric acid test. For example, ratios of the stabilized-plus-sensitized corrosion rate to the annealed corrosion rate for heat FI9A were 1.1 in the nitric acid test and 1.3 in the nitric-hydrofluoric acid test. (When heat FI9A was stabilized for 4 hours at 1600 F, water quenched, agglomerated sigma phase was formed in the grain boundaries (see Figure 2C). A sensitizing treatment of 1 hour at 1300 F following stabilization at 1600 F produced no additional sigma phase. Figure 7 shows that the behavior of stabilized-plus-sensitized specimens of heat FI9A containing agglomerated sigma phase, for practical purposes, was identical to that of the annealed specimens in both corrosion tests.

The electrolytic oxalic acid etching test produced a relatively shallow ditch structure on stabilized-plus-sensitized specimens of heat FI9A containing agglomerated sigma phase. (See Figure 8C.) If such a
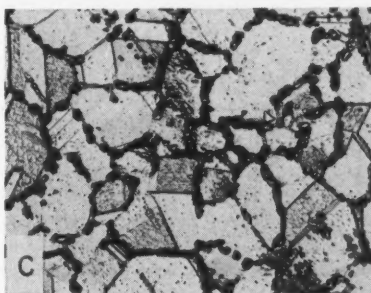
Figure 8—Etch structures for Heat FI9A of Type 316L stainless steel produced by the electrolytic oxalic acid etching test, 250X.

(A)—Commercially annealed; step structure.

(B)—Sensitized 1 hour at 1300 F, water quenched; dual structure (mild).

(C)—Stabilized 4 hours at 1600 F, water quenched and sensitized 1 hour at 1300 F, water quenched; ditch structure (relatively shallow ditching).

ditch structure is obtained in the oxalic acid etch testing of Types 304 or 304L stainless, it indicates damaging carbide precipitation and the steel must be submitted to the nitric acid test for further evaluation.[5] However, in the present case, even though heat FI9A showed a ditch structure in the stabilized-plus sensitized condition, it did not undergo intergranular corrosion in either the nitric or the nitric-hydrofluoric acid test. This behavior is due to the fact that the agglomerated sigma phase, which was responsible for the ditch structure, had no effect on the intergranular corrosion resistance in the two corrosion tests.
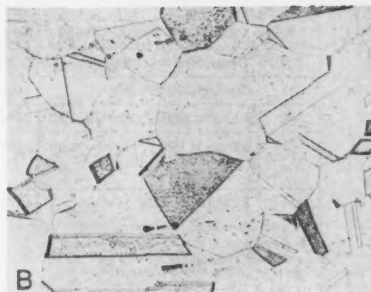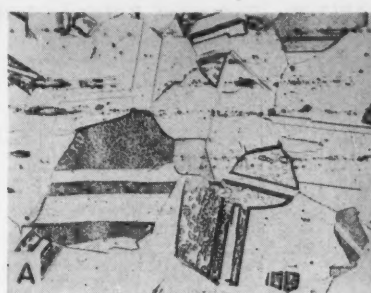
Annealed Condition. In the annealed condition, the three heats of Type 316L stainless steel showed normal corrosion behavior in both the nitric acid and nitric-hydrofluoric acid tests. There was no evidence of intergranular attack on annealed specimens in either test. The electrolytic oxalic acid etch structures for the three Type 316L heats in the annealed condition were all step structures similar to that shown in Figure 8A.

TABLE 5—Data for Tungsten Inert-Arc Welded Type 316L Stainless Steel Obtained in Standard Laboratory Tests for Susceptibility to Intergranular Corrosion

Heat Number	Heat Treatment Code[1]	Boiling 65% Nitric Acid Test[2]		10% Nitric-3% Hydrofluoric Acid Test[3]	
		Rate Inches/ Month	Ratio[4]	Rate Inches/ Month	Ratio[4]
FI9A	4	0.00141*	2.4	0.16	0.8
FI4A	4	0.0062*	5.3	1.03[5]	1.4
FI2A	4	0.0032*	4.2	0.47	0.9

* Severe preferential attack of an interdendritic nature occurred on the weld metal.
[1] Heat-treatment code and microstructure of these samples are the same as those given in Table 2.
[2] Three-period test totaling 232 hr in a multisample tester.
[3] Five ½ hr periods.
[4] Ratio of corrosion rate for welded sample to that for annealed sample (corrosion rates for annealed samples are given in Table 5.
[5] Rate of general or uniform attack on weld metal was greater than that on base plate. (No interdendritic attack of weld metal.)

TABLE 6—Corrosion Rates in Inches/Month for Types 316 and 316L Stainless Steel Tested in Various Acid Media

Laboratory Heat Number	Heat Treatment Code	Condition of Heat Treatment	Standard Nitric Test	10% Nitric-3% Hydrofluoric at 80 C	0.5% Sulfuric at 50 C	0.5% Sulfuric at Boiling	10% Sulfuric at Boiling	30% Sulfuric at 35C	20% Acetic at Boiling[4]	85% Lactic at Boiling	10% Formic at Boiling	45% Formic at Boiling	10% Oxalic at Boiling	50% Phosphoric at Boiling	70% Phosphoric at Boiling	20% Citric at Boiling
MY316	1	Commercially Annealed	0.00089	0.31	0.00001[1]	0.0026	0.050	0.00104	0.00002	0.0029[1]	0.0037	0.0063	0.0058	0.0013	0.018	0.00002[3]
	2	2 hours at 1250 F, water quenched	0.097	6.9	0.0018	0.024	1.08	0.147	0.00055	0.0030	0.0040	0.0070	0.011	0.0039	0.034	0.00004[3]
F14A	1	Commercially Annealed	0.00116	0.72	....	0.0036	1.33	....	0.00006	0.0030	....	0.011	0.0059	....	....	....
	2	1 hour at 1300 F, water quenched	0.035	0.63	....	0.0033	1.35	....	0.00006	0.0032	....	0.0099	0.0055	....	....	....
	4	Tungsten inert-arc welded	0.00108	1.03	....	0.0036	1.36	....	0.00006	0.0032	....	0.012	....	....	....	....
F12A	1	Commercially Annealed	0.00077	0.51	....	0.0051	0.96	....	0.00004	0.0030	....	0.011	0.0067	....	....	....
	2	1 hour at 1300 F, water quenched	0.024	0.56	....	0.0050	1.20	....	0.00003	0.0040[1]	....	0.0099	0.0072	....	....	....
	4	Tungsten inert-arc welded	0.0074	0.47	....	0.0056	0.99	....	0.00002	0.0032	....	0.0094	....	....	....	....
F19A	1	Commercially Annealed	0.00059	0.20	....	0.0031	0.075	....	0.00002	0.000008[2]	....	0.0066	0.0065	0.00091	....	0.00001[3]
	2	1 hour at 1300 F, water quenched	0.080	0.20	....	0.0032	0.085	....	0.00002	0.0030	....	0.0074	0.0067	0.00095	....	0.00001[3]
	3	4 hours at 1600 F, water quenched + 1 hour at 1300 F, water quenched	0.00066	0.27	....	0.0035	0.099	....	0.00003	0.000008[2]	....	0.0070	0.0066	0.00090	....	0.00002[3]
	4	Tungsten inert-arc welded	0.0066	0.16	....	0.0036	0.088	....	0.00003	0.0032	....	0.0086	....	....	....	....

[1] Sample only corroded during one test period.

[2] Sample did not corrode during any test period. Bulk of corrosion was due to activation treatments.

[3] Sample had a definite, but almost negligible, corrosion rate.

[4] All samples tested except MY316-2 had extremely low corrosion rates, but there was definite evidence of very light corrosive attack.

Length of Test and Test Period

Test Environment	Test Period	Total Test Time, hr
Standard Nitric Acid Test	Five 48-hr. periods	240 hr.
10% Nitric-3% Hydrofluoric Acid-80 C	Five ½-hr. periods	2½ hr.
0.5% Sulfuric Acid-50 C	Fifteen 24-hr. periods	360 hr.
0.5% Sulfuric Acid-Boiling	Eight 24-hr. periods	192 hr; 312 hr. for MY316-1 and 2
10% Sulfuric Acid-Boiling	Five 1-hr. periods	5 hr.
30% Sulfuric Acid-35 C	Three 24-hr. periods	72 hr.
20% Acetic Acid-Boiling	Nine 24-hr. periods	216 hr; 504 hr. for MY316-1 and 2
85% Lactic Acid-Boiling	Four 24-hr. periods	96 hr; 192 hr. for MY316-1 and 2
10% Formic Acid-Boiling	Four 4-hr. periods	16 hr.
45% Formic Acid-Boiling	(Periods varied from ½ to 24-hr.)	60 hr.
10% Oxalic Acid-Boiling	Five 24-hr. periods	120 hr.
50% Phosphoric Acid-Boiling	Five 24-hr. periods	120 hr; 264 hr. for MY316-1 and 2
70% Phosphoric Acid-Boiling	Seven 4-hr. periods	28 hr.
20% Citric Acid-Boiling	(Periods varied from 24 to 288 hr.)	240 hr; 1082 hr. for MY316-1 and 2

Welded Condition. Tungsten inert-arc welded specimens of three Type 316L heats underwent severe preferential attack of the weld metal in the boiling 65 percent nitric acid test[3] but not in the 10 percent nitric-3 percent hydrofluoric acid test. Ratios of the corrosion rate in the welded condition to the rate in the annealed (unwelded) condition varied from 2.4 to 5.3 in the nitric acid test and from 0.8 to 1.4 in the nitric-hydrofluoric acid test (see Table 5).

The high corrosion rates for welded specimens in the nitric acid test were due to severe interdendritic corrosion of the weld metal, i.e., preferential attack which reveals the original dendritic or cast structure of the weld metal. This interdendritic attack is believed, for two reasons, to be caused by the presence of sigma phase in the weld metal. First, the absence of such preferential attack in the nitric-hydrofluoric acid test indicates that carbide precipitation was not responsible. Secondly, laboratory reannealing of the welded specimens removed any tendency for interdendritic attack of the weld metal in the nitric acid test. Similar results have been previously reported.[8]

None of the welded specimens showed evidence of severe intergranular corrosion and grain-dropping in the heat-affected zone of the base plate in either corrosion test. This observation agrees with earlier work[8,9] and indicates that under these welding conditions any sigma phase formed in the heat-affected zone was insufficient to

[3] The nitric acid tests were made in the multi-sample tester[2] instead of flasks to avoid spurious attack on the base plate. When severe corrosion of the weld metal occurs, contamination of the nitric acid solution by chromium ions is possible in flask testing. If the concentration of chromium ion is high enough, these ions can cause severe intergranular attack and grain-dropping on areas of the base plate completely removed from the heat-affected zone of the weld.

damage the nitric acid corrosion resistance. The electrolytic oxalic acid etch structure of the heat-affected zones of all the weld specimens was step in nature, i.e., no microscopically visible phase was formed in the grain boundaries.

Summary of Results for Standard Laboratory Tests.

1. The boiling 65 percent nitric acid test, the 10 percent nitric-3 percent hydrofluoric acid test, and the electrolytic oxalic acid etching test were all sensitive to the presence of a continuous network of chromium carbides in the grain boundaries of Type 316 stainless steel. Such a carbide network resulted in severe intergranular corrosion, grain-dropping and accelerated corrosion rates in both the nitric and the nitric-hydrofluoric acid tests. The presence of the carbide network was readily revealed by the electrolytic oxalic acid etching test as a ditch structure, with most of the grains completely encircled by carbides.

2. The presence of a continuous grain-boundary network of sigma phase in Type 316L stainless steel caused severe intergranular corrosion, grain-dropping and very high corrosion rates in the standard nitric acid test. A similar network of sigma phase had no effect on the corrosion of Type 316L stainless steel in the nitric-hydrofluoric acid test. The oxalic acid

etch structures for Type 316L stainless steel containing a continuous grain-boundary network of sigma phase varied from step to mild dual in nature.

3. Agglomerated sigma phase present as separate discrete particles in the grain boundaries of Type 316L stainless steel had little or no effect on the corrosion behavior in either the nitric acid test or in the nitric-hydrofluoric acid test. The oxalic acid etch structure of Type 316L stainless steel containing agglomerated sigma phase was a ditch structure with relatively shallow ditching.

4. The weld metal in tungsten inert-arc welded specimens of Type 316L stainless steel underwent severe preferential attack in the nitric acid test, probably due to the presence of sigma phase. In the nitric-hydrofluoric acid test, similarly welded specimens showed no tendency for preferential attack on the weld metal.

Other laboratory corrosion tests in acid media

Type 316 Stainless Steel (Effect of Chromium Carbides). The intergranular corrosion behavior of Type 316 stainless steel having a continuous network of grain-boundary carbides is discussed below for those twelve acid media listed in Table 3. The discussion has been divided into sections dealing with those 10 media which

Boiling 65 percent nitric acid, 240 hours

Boiling 50 percent phosphoric acid, 264 hours

Boiling 70 percent phosphoric acid, 28 hours

0.5 percent sulfuric acid at 50 C, 360 hours

Boiling 0.5 percent sulfuric acid, 312 hours

10 percent nitric–3 percent hydrofluoric acid, 2.5 hours

Boiling 85 percent lactic acid, 192 hours

Boiling 20 percent acetic acid, 504 hours

Boiling 10 percent oxalic acid, 120 hours

Boiling 10 percent sulfuric acid, 5 hours

30 percent sulfuric acid at 35 C, 72 hours

Figure 10—Cross-Sectional views of intergranular attack on Type 316 stainless steel (Heat MY316) sensitized for 2 hours at 1250 F, water quenched and exposed in various acid media, 50X.

Figure 11—Corrosive attack on Type 316 stainless steel (Heat MY316) exposed for 1082 hours in boiling 20 percent citric acid, 250X. Sensitized 2 hours at 1250 F, water quenched. Corrosion rate: 0.00004 in./mo.

Figure 12—Corrosion of Type 316 stainless steel (Heat MY316) in boiling 0.5 percent sulfuric acid.

produced severe intergranular attack and grain-dropping and those two media which produced only intergranular etching. The corrosion rates for Type 316 stainless steel in all of the acid media are given in Table 6.

Media Producing Severe Intergranular Attack and Grain Dropping. General Results: The following 10 corrosive environments caused severe intergranular attack and grain-dropping on sensitized Type 316 stainless steel containing a continuous carbide network in the grain boundaries: 0.5 percent sulfuric acid at 50 C, 30 percent sulfuric acid at 35 C, and boiling solutions of 0.5 percent sulfuric acid, 10 percent sulfuric acid, 85 percent lactic acid, 20 percent acetic acid, 10 percent oxalic acid, 50 percent phosphoric acid, 70 percent phosphoric acid and 20 percent citric acid.

Table 7 summarizes the intergranular corrosion behavior of sensitized Type 316 stainless steel in those acid media listed above. For comparison purposes, the data for the boiling 65 percent nitric acid test and the 10 percent nitric-3 percent hydrofluoric acid test have also been included. In Table 7 the ratio of the sensitized corrosion rate to the annealed corrosion rate

has been used to provide an index of the relative severity of the intergranular corrosion compared to the general corrosion. The time required to produce varying degrees of grain-dropping is used to show the progress of intergranular attack in the various media. Where severe grain-dropping caused a measurable decrease in the dimensions of the corrosion specimen, this is indicated in the column headed as metal removed by grain dropping.

Also given in Table 7 is the depth of intergranular attack as microscopically measured on the cross-section of the corrosion specimen at the completion of the test. The total depth of intergranular attack was obtained from the sum of the measured depth of intergranular attack on the sample and one-half of the decrease in sample thickness due to grain-dropping. For comparison, the total depth of attack also was calculated by multiplying the average corrosion rate (as determined from weight-loss measurements) by the total test time. As expected, the calculated total depth of attack generally was much less than the measured total depth of attack because of the penetration of the intergranular attack into the corrosion specimen. The degree of intergranular
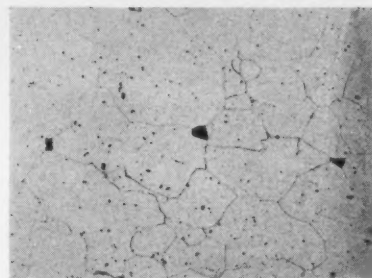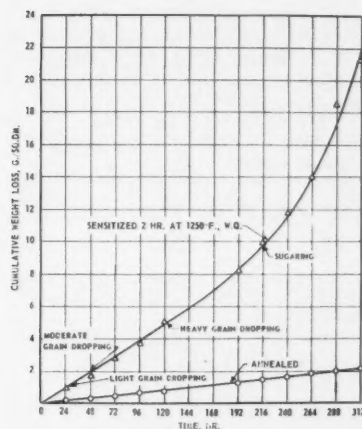
penetration for each of the acid environments in Table 7 (except boiling 20 percent citric acid) is pictorially compared in Figure 10.

Factors Determining the Severity of Intergranular Corrosion: The data in Table 7 show the wide variation in the degree of grain-dropping caused by intergranular corrosion in the different environments. The grain-dropping ranged from only a few dropped grains to a sugary condition where the grains could be dislodged easily by rubbing the surface of the specimen. The amount of grain-dropping depended upon two factors: the rate of intergranular attack (and consequently the length of test) and the relative severity of the intergranular attack compared to the general attack.

For example, in boiling 20 percent citric acid, where the rate of intergranular attack was low, the grain-dropping was still light in nature after 1000 hours of testing (see Figure 11). On the other hand, the rate of intergranular attack in boiling 70 percent phosphoric acid was quite high, but this attack was outdistanced by a more severe general attack. Consequently, only a few fragments of grains were dislodged in the initial stages of this test. The remaining grains were largely corroded away by the general attack before they could be undermined and dropped from the surface by the intergranular attack.

| 1 hour | 25 hours | 73 hours |
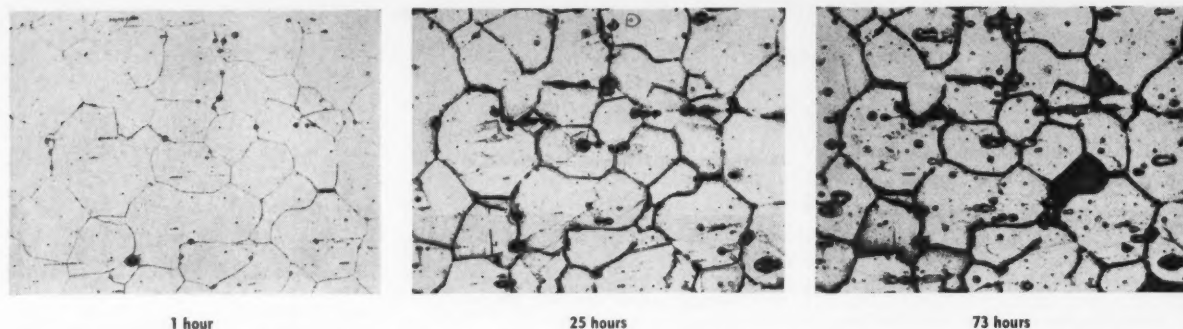
Figure 13—Progressive corrosion of Type 316 stainless steel (Heat MY316) in boiling 0.5 percent sulfuric acid, 250X. Sensitized 2 hours at 1250F, water quenched; corrosion rate: 0.024 in./mo.

TABLE 7—A Summary of the Intergranular Corrosion Behavior of Sensitized Type 316 Stainless Steel (Heat MY316) Containing a Continuous Grain Boundary Network of Chromium Carbides

| Description of Corrosion Test | | | Corrosion Rate, Inches/Month | | Ratio of Sensitized to Annealed Rate | Time Required to Drop The Following Number of Grains,[2] hr. | | | | Metal Removed by Grain Dropping,[4] mil | Depth of Intergranular Attack[5] mil | Total Depth of Attack (Measured)[6] mil | Total Depth of Attack (Calculated)[7] mil |
Solution and Concentration	Temperature	Length of Test, hr.	Annealed	Sensitized[1]		Few	Moderate	Large	Sugaring[3]				
Sulfuric acid												
0.5%	50°C.	360	0.000018	0.0018	180	72	240	....	....	..	9	9	0.9
0.5%	Boiling	312	0.0026	0.024	9	24	48	120	216	..	32	32	10
10%	Boiling	5	0.050	1.08	22	....	0.5	1.5	2.5	4	13	17	8
30%	35°C.	72	0.00104	0.147	141	....	....	....	24	17	12	29	15
Phosphoric acid												
50%	Boiling	264	0.00126	0.0039	3	82	178	250	....	..	2.4	2.4	1.4
70%	Boiling	28	0.018	0.034	2	10	....	....	....	..	1.0	1.0	1.0
10% Oxalic acid	Boiling	120	0.0058	0.011	2	5	30	54	....	..	1.6	1.6	1.8
20% Acetic acid	Boiling	504	0.000028	0.00055	27	72	288	432	....	..	3.7	3.7	0.4
85% Lactic acid	Boiling	192	(0.0029)[9]	0.0030	(1)[9]	30	54	....	....	..	1.6	1.6	0.8
20% Citric acid	Boiling	1082	0.00000210	0.00000410	2	462	....	....	....	..	...	...	...
65% Nitric acid	Boiling	240	0.00089	0.097	109	....	48	....	96	28	6	34	32
10% Nitric—3% Hydrofluoric acid.	80°C.	2.5	0.31	6.9	22	....	....	0.5	1	13	13	26	24

[1] Sensitized 2 hr 1250 F, water quenched.
[2] Summary of grain dropping on sensitized samples due to intergranular attack.
[3] Sugaring is that surface condition where the grains can be easily removed by rubbing the sample.
[4] In the case of four tests, the intergranular attack and resulting grain dropping was severe enough to appreciably decrease the sample dimensions. The figures in this column represent one-half of the decrease in thickness of the samples.
[5] The depth of intergranular attack as measured microscopically on a cross section of the corroded sample.

[6] The measured depth of attack is the sum of one-half the decrease in sample thickness and the depth of intergranular attack as measured microscopically.
[7] This depth of attack was calculated from the corrosion rate for the sensitized sample and the total time on test.
[8] These corrosion rates represent little or no attack on the sample.
[9] The annealed sample corroded for only one 24-hr period and then became passive. The ratio is based on this one 24-hr rate.
[10] Both the annealed and sensitized samples had very small, but definite corrosion rates.

The role of general attack in governing the degree of intergranular deterioration is emphasized by a comparison of the corrosion behavior in boiling 50 percent phosphoric acid with that in boiling 70 percent phosphoric acid. The rate of general attack on Type 316 stainless steel in boiling 50 percent phosphoric acid was only 7 percent of that in boiling 70 percent phosphoric acid (compare corrosion rates of heat MY316 for annealed condition in Table 6). Because of this decrease in general attack, a large number of grains were dropped from the sensitized specimen in boiling 50 percent phosphoric acid while only a few grain fragments were dropped in boiling 70 percent phosphoric acid.

Other investigators have also recognized that the degree of general attack may determine whether or not severe intergranular corrosion is observed in laboratory corrosion testing. For example, Binder and Brown[9] found that sensitized Types 316 and 317 stainless steel were intergranularly corroded in air-free 10 percent sulfuric acid at 70 C; sensitized Type 304 stainless steel (having less corrosion resistance than Types 316 or 317) underwent only general attack in the same environment. They state that while "the over-all corrosion resistance of the steel to corrosion in this medium is increased by the addition of molybdenum, the corrosion is accelerated at the grain boundaries, if these boundaries are sensitive as a result of carbide precipitation." Nielsen[10] reported a similar experience for tests made in boiling 3 percent sulfuric acid; a sensitized Type 304 stainless steel underwent mainly general attack while a sensitized Type 316 stainless steel underwent severe intergranular corrosion and grain-dropping.

Progressive Corrosion Behavior: Curves of weight loss vs testing time for those media causing intergranular corrosion of sensitized Type 316 stainless steel were roughly of two general types.

In the first type, the curves were similar to those shown in Figures 4 and 5 for the boiling 65 percent nitric acid test and the 10 percent nitric-3 percent hydrofluoric acid test. Laboratory corrosion tests producing this type of curves included the following: 0.5 percent sulfuric acid at 50 C, boiling 0.5 percent sulfuric acid, boiling 10 percent sulfuric acid, 30 percent sulfuric acid at 35 C, boiling 20 percent acetic acid and boiling 50 percent phosphoric acid. For example, Figure 12 shows the corrosion behavior of Type 316 stainless steel in boiling 0.5 percent sulfuric acid. Note that the curve for the sensitized specimen increased in slope as grain-dropping occurred due to intergranular corrosion (Figure 13 illustrates the progressive intergranular attack on the surface of the sensitized specimen). The curve for the annealed specimen was linear throughout the test with a much lower slope than
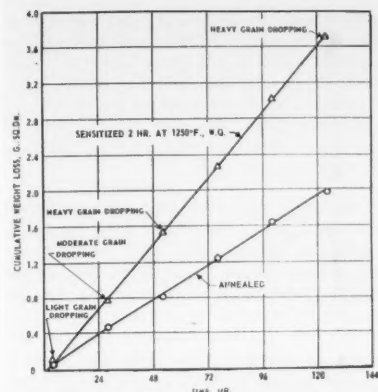
Figure 14—Corrosion of Type 316 stainless steel (Heat MY316) in boiling 10 percent oxalic acid.

the curve for the sensitized specimen. Curves for the other environments listed above were similar to the ones shown in Figure 12.

The second type of corrosion curves consisted of those where both the sensitized and the annealed specimens corroded at a constant rate, thereby producing linear weight loss vs time corrosion curves. Curves of this type were obtained for Type 316 stainless steel tested in boiling 10 percent oxalic acid, boiling 85 percent lactic acid, and boiling 70 percent phosphoric acid. Figure 14 illustrates the corrosion curves for Type 316 exposed to boiling 10 percent oxalic acid. Note that the curve for the sensitized specimen is linear despite the occurrence of heavy grain-dropping. This linearity is due to severe general attack which accompanied the intergranular attack and grain-dropping. (The relative severity of the general attack is indicated by the steep slope of the curve for the annealed specimen). Figure 15 compares the corrosive attack on both annealed and sensitized Type 316 stainless steel in boiling 10 percent oxalic acid. Note how the severe general attack has increased the width of the grain-boundary attack.

In those acid media in which sensitized Type 316 stainless steel corroded at an approximately constant rate, the intergranular attack never proceeded very far ahead of the corroding surface. For example, the measured depth of intergranular attack on sensitized Type 316 stainless steel tested in boiling solutions of 10 percent oxalic acid, 85 percent lactic acid and 70 percent phosphoric acid never exceeded 1 to 1.5 mils (see Table 8 and Figure 10).

Media Producing Integranular Etching. Only two of the acid media listed in Table 3 failed to produce severe intergranular attack and grain-dropping on sensitized Type 316 stainless steel. These were the boiling 10 percent and 45 percent formic acid environments. Boiling 45 percent formic acid produced light intergranular etching on the sensitized specimen in the early stages of testing. However, as shown in Figure 16, this intergranular etching was overtaken and obliterated by a more severe general attack. Nielsen[10] observed a similar pattern of behavior for sensitized Type 316 stainless steel in boiling 3 percent hydrochloric acid.
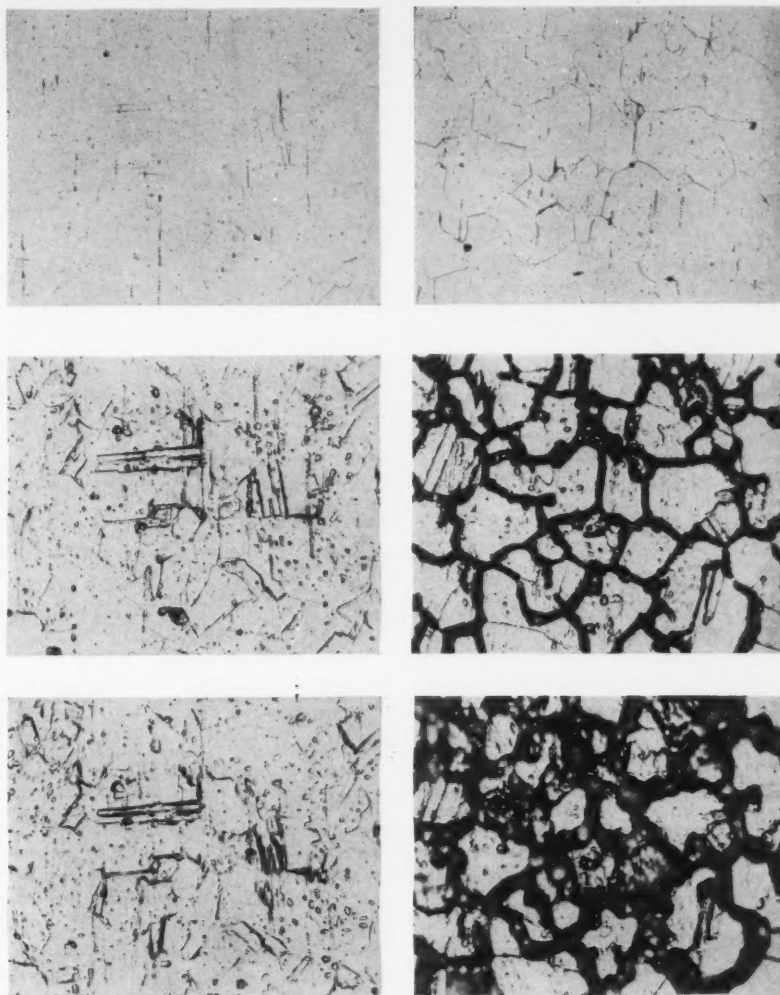
Figure 15—Progressive corrosion of Type 316 stainless steel (Heat MY316) in boiling 10 percent oxalic acid, 250X. Left figures: commercially annealed; corrosion rate 0.0058 in./mo. Right figures: sensitized 2 hours at 1250 F, water quenched; corrosion rate: 0.011 in./mo. Exposure times: top row, 1 hour; middle row, 29 hours; bottom row, 53 hours.

TABLE 8—Data for Field Corrosion Tests of Type 316L Stainless Steel in a 30% Nitric-14% Adipic Acid Solution at 110 C

Heat Number	Heat Treatment Code	Condition of Heat Treatment	Corrosion Rate, Inches/Month	
			30% Nitric-14% Adipic Acid Solution at 110C (Seven-Month Exposure)	Boiling 65% Nitric Acid Test[1] (240-hr Exposure)
F19A.........	1	Commercially Annealed	0.00010	0.00059
	2	1 hr. 1300°F., W.Q.[2]	0.00132	0.080
	3	4 hr. 1600°F., W.Q. + 1 hr. 1300°F., W.Q.[3]	0.00011	0.00066
	4	Tungsten inert-arc welded	0.00036	0.00141
F14A.........	1	Commercially Annealed	0.00018	0.00116
	2	1 hr. 1300°F., W.Q.[2]	0.0022	0.035
	4	Tungsten inert-arc welded	0.00031	0.0062

[1] These data were included for comparison. Flask tests were used except for the welded specimens which were tested in a multisample tester.
[2] Specimens had a continuous grain boundary network of sigma phase. W.Q. = Water quenched.
[3] Specimen had agglomerated sigma phase in the grain boundaries.
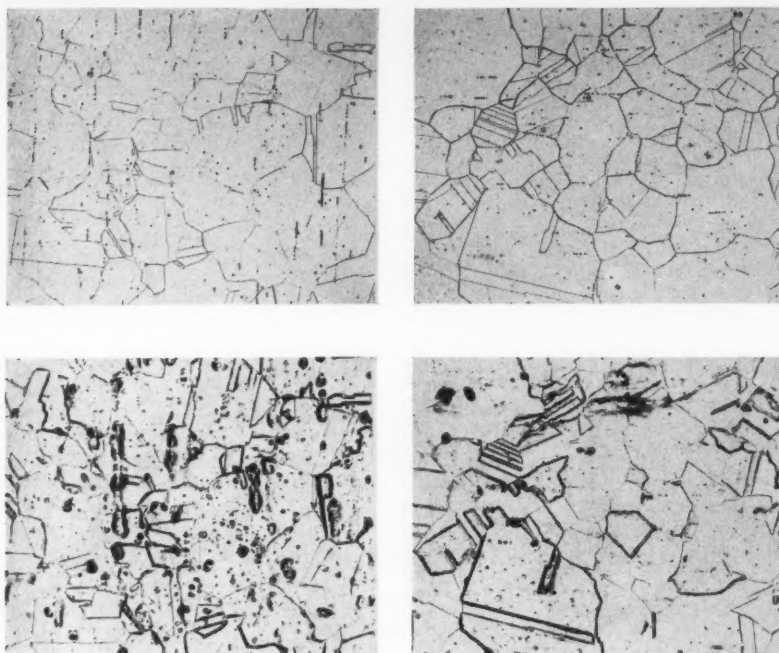
Figure 16—Progressive corrosion of Type 316 stainless steel (Heat MY316) in boiling 45 percent formic acid, 250X. Left figures: commercially annealed; corrosion rate: 0.0063 in./mo. Right figures: sensitized 2 hours at 1250 F, water quenched; corrosion rate: 0.0070 in./mo. Exposure times: top, 1 hour; bottom, 25 hours.

The tests in boiling 10 percent formic acid were made to determine if a reduction in the rate of general corrosion would accentuate the intergranular attack. Despite a twofold decrease in the general corrosion rate (compared to boiling 45 percent formic acid), the attack on sensitized Type 316 stainless steel in boiling 10 percent formic acid never exceeded light intergranular etching.

Type 316L Stainless Steel (Effect of Sigma Phase).

Effect of Continuous Grain-Boundary Network of Sigma Phase. None of the 12 acid media listed in Table 3 intergranularly attacked those specimens of Type 316L stainless steel containing a continuous grain-boundary network of sigma phase (no carbide network was present). These specimens included samples of heats FI9A, FI2A and FI4A which had been sensitized for 1 hour at 1300 F, water quenched. The pattern of corrosive attack on all of these specimens was predominately one of general corrosion, rather than intergranular. This is shown by the photomicrographs in Figures 17B and 18A of the progressive corrosion of sensitized Type 316L stainless steel in boiling 0.5 percent sulfuric acid and in boiling 50 percent phosphoric acid, respectively. Note the similarity in the pattern of corrosive attack on the annealed and the sensitized specimens (compare Figure 17A and 17B). In both cases, the twins and steps associated with an annealed structure are predominant; the sharply delineated grain boundaries associated with intergranular attack are absent.

The corrosion rates given in Table 6 show that a continuous grain-boundary

network of sigma phase had no effect on the corrosion of Type 316L stainless steel in any of the acid media other than nitric (Compare the corrosion rates for heats FI9A, FI2A and FI4A in the sensitized condition (1 hour at 1300 F, water quenched) with those in the annealed condition.)

Effect of Agglomerated Sigma Phase in the Grain Boundaries. Agglomerated sigma phase present as separate discrete particles in the grain boundaries of Type 316L stainless steel had little or no effect on the corrosion in those acid media listed in Table 3. In most of these media, the presence of agglomerated sigma phase caused light to heavy intergranular etching of Type 316L stainless steel. This etching never developed into serious intergranular attack. Figures 17C and 18B illustrate the pattern of corrosive attack on samples of Type 316 stainless steel containing agglomerated sigma phase. Note that the grain boundaries in these cases are fairly well defined as a result of light intergranular etching. The corrosion rates in Table 6 show that agglomerated sigma phase had little or no effect on the corrosion resistance of Type 316L stainless steel in any of the acid media including nitric. (Compare the corrosion rates for heat FI9A in the stabilized-plus-sensitized condition (4 hours 1600 F, water quenched + 1 hour 1300 F, water quenched) with those in the annealed condition.)

The 30 percent sulfuric acid at 35 C, was the one corrosive environment in which sigma phase was reported to have seriously decreased the corrosion resistance of stainless steel.[5, 6] A total of four Type 316L heats containing agglomerated sigma phase were tested in this environment. Only one of the four heats showed

any change in corrosion behavior due to the sigma phase. In this heat of steel the agglomerated sigma phase upset the normal self-passivating tendency of the steel, causing it to corrode both generally and intergranularly. However, the intergranular attack was not sufficient to produce grain-dropping.

Welded Type 316L Stainless Steel. The welded samples of Type 316L stainless steel exposed to those acid media listed in Table 3 showed no evidence of either severe preferential (interdendritic) attack on the weld metal or severe intergranular attack on the heat-affected zone of the weld. In some of the tests, the general attack on the weld metal was more severe than that on the base plate of welded samples of heats FI2A and FI4A. However, in no case was the attack severe enough to cause an appreciable difference between the corrosion rate for the welded sample and that for the annealed sample. This observation is verified by corrosion data given in Table 6 for tungsten inert-arc welded samples of heats FI9A, FI2A and FI4A.

Correlation Between Standard Laboratory Tests for Susceptibility to Intergranular Corrosion and Intergranular Corrosion Tests in Other Acid Media

Effect of Chromium Carbides. Where a continuous network of grain-boundary carbides was present in sensitized Type 316 stainless steel, both the boiling 65 percent nitric acid test and the 10 percent nitric-3 percent hydrofluoric acid test produced severe intergranular attack and grain-dropping. This type of behavior was repeated when samples of sensitized Type 316 stainless steel containing a similar carbide network were exposed to 10 of the 12 acid media listed in Table 3. The principal difference between the corrosion behavior in the two standard laboratory tests and that in the other 10 acid environments was the degree of intergranular deterioration. Thus, both the standard nitric acid test and the nitric-hydrofluoric acid test offer a reliable criterion of the susceptibility of austenitic stainless steels to intergranular attack in other acid media due to the presence of grain-boundary carbides.

Effect of Sigma Phase
Continuous Grain-Boundary Network of Sigma Phase. Of all the laboratory testing media evaluated, standard and otherwise, only the boiling 65 percent nitric acid test was sensitive to a continuous grain-boundary network of sigma phase. The presence of such a network in Type 316L stainless steel caused severe intergranular attack and grain-dropping in the standard nitric acid test but had no effect on the corrosion in the nitric-hydrofluoric acid test or in any of the acid media listed in Table 3.

Agglomerated Sigma Phase. In general, agglomerated sigma phase present as separate discrete particles in the grain boundaries had little or no effect on the corrosion of Type 316L stainless steel in either of the two standard laboratory tests or in any of the acid corrosion tests listed in Table 3. In the case of one heat of Type 316L
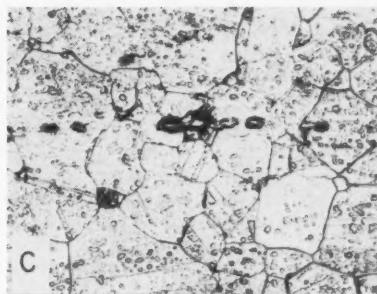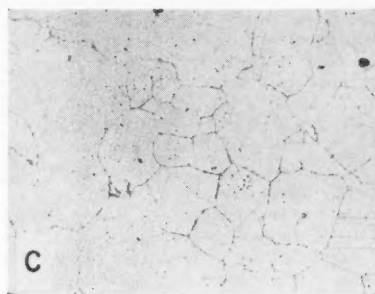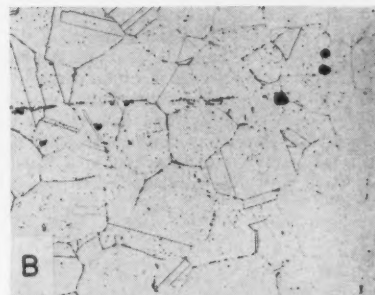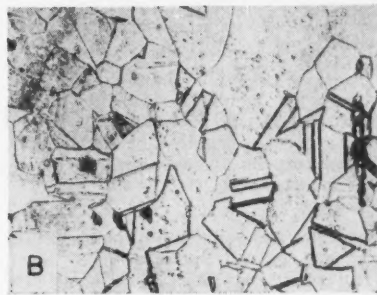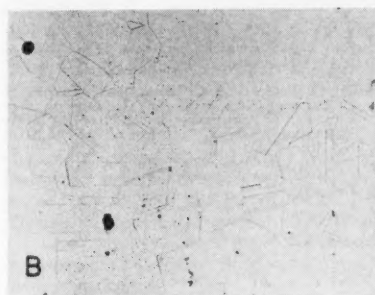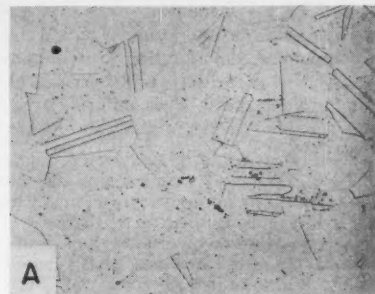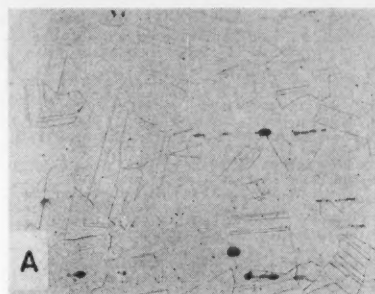
Figure 17—Progressive corrosion of Type 316L stainless steel (Heat FI9A) in boiling 0.5 percent sulfuric acid, 250X. Exposure times: left figures, 1 hour; right figures, 25 hours.

(A)—Commercially annealed; corrosion rate: 0.0031 in./mo.

(B)—Sensitized 1 hour at 1300 F, water quenched; corrosion rate: 0.0032 in./mo.

(C)—Stabilized 4 hours at 1600 F, water quenched + sensitized 1 hour at 1300 F, water quenched; corrosion rate: 0.0035 in./mo.

Figure 18—Corrosive attack on Type 316L stainless steel (Heat FI9A) exposed 30 hours in boiling 50 percent phosphoric acid, 250X.

(A)—Sensitized 1 hour at 1300 F, water quenched; corrosion rate: 0.00095 in./mo.

(B)—Stabilized 4 hours at 1600 F, water quenched + sensitized 1 hour at 1300 F, water quenched; corrosion rate: 0.00090 in./mo.

stainless steel exposed to 30 percent sulfuric acid at 35 C, the presence of agglomerated sigma phase upset the natural passivity of the steel and severe corrosion resulted.

Welded Type 316L Stainless Steel. The boiling 65 percent nitric acid test was the only corrosive environment found to be sensitive to sigma phase formed in the welding of Type 316L stainless steel. The nitric acid test produced severe interdendritic attack on the weld metal of tungsten inert-arc welded samples of Type 316L stainless steel. This type of attack did not occur in the nitric-hydrofluoric acid test or in any of the acid media listed in Table 3.

Conclusions Regarding Sigma Phase and Standard Laboratory Corrosion Tests. The boiling 65 percent nitric acid test is not a reliable criterion of the susceptibility of Type 316L stainless steel to intergranular attack in other acid media when a continuous grain-boundary network of sigma phase is present. The 10 percent nitric-3

percent hydrofluoric acid test affords a reliable gage of the intergranular corrosion behavior of Type 316L stainless steel in acid media other than nitric. However, this test has not been standardized for use as a routine evaluation method.

Field Corrosion Tests on Type 316L Stainless Steel

Table 8 gives the results of a seven-month field exposure of heats FI9A and FI4A of Type 316L stainless steel in a 30 percent nitric-14 percent adipic acid solution at 110 C. The standard nitric acid test data for these steels in similar conditions of heat treatment are included for comparison purposes.

In general, the pattern of corrosion behavior of Type 316L stainless steel in the 30 percent nitric-14 percent adipic acid solution at 110 C was similar to that observed in the boiling 65 percent nitric acid test. A continuous grain-boundary network of sigma phase (produced by sensitizing 1 hour at 1300 F, water quenched) caused

severe intergranular attack and grain-dropping in the nitric-adipic acid exposure. The presence of agglomerated sigma phase in Type 316L stainless steel had little or no effect on the corrosion in the nitric-adipic acid solution. (Compare the corrosion rate for heat FI9A after a heat-treatment of 4 hours 1600 F, water quenched + 1 hour at 1300 F, water quenched, with that for the annealed condition.) The tungsten inert-arc welded specimens of both heats (FI9A and FI4A) underwent severe interdendritic attack on the weld metal in the nitric-adipic acid field exposure.

Because of the lower nitric acid concentration of the nitric-adipic acid mixture, the actual corrosion rates for Type 316L stainless steel in 30 percent nitric-14 percent adipic acid solution at 110 C were less than those in the boiling 65 percent nitric acid test.

The above results indicate that where severe nitric acid service is involved, the standard nitric acid test is a reliable criterion of the susceptibility of Type 316L stainless steel to intergranular corrosion. Stated another way, if sigma phase is present in such a form as to damage the corrosion resistance of Type 316L stainless steel in the boiling 65 percent nitric acid test, then such sigma phase is also likely to have a deleterious effect on the corrosion resistance in plant environments involving hot nitric acid solutions.

Summary

1. The presence of a continuous grain-boundary network of chromium carbides

caused Type 316 stainless steel to be susceptible to severe intergranular attack and accompanying deterioration in numerous acid media in addition to nitric acid. Among these media were sulfuric, lactic, acetic, oxalic, citric and phosphoric acids.

2. As far as could be established, sigma phase in Type 316L stainless steel did not cause intergranular deterioration in any of the acid media studied other than nitric acid. The presence of a continuous grain-boundary network of sigma phase caused severe intergranular corrosion of Type 316L stainless steel in the standard nitric acid test.

3. Based on Result 2 above, the standard nitric acid test is not a fair measure of the susceptibility of Type 316L stainless steel to intergranular attack in other corrosive environments. On the other hand, where Type 316L stainless steel is to be used for service involving hot nitric acid or nitric acid mixtures, the standard nitric acid test can be usefully applied.

4. The danger of intergranular attack in service, due to the presence of a carbide network in austenitic stainless steel, has again been emphasized. Therefore, use of the standard nitric acid test or other suitable tests to screen materials such as Types 304, 304L and 316 stainless steel for freedom from harmful carbide precipitation is justified.

5. The results of this investigation emphasize the need for development of an intergranular corrosion test capable of screening Type 316L stainless steel for freedom from harmful carbide precipitation without being affected by the simultaneous presence of sigma phase. The 10 percent nitric-3 percent hydrofluoric acid test might be standardized for this purpose.

Acknowledgments

Particular thanks are due M. H. Brown, W. B. DeLong and J. R. Auld, who helped in planning the investigation, and to E. D. Nicholson, who assisted with most of the corrosion tests.

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Selecting Corrosion and Scale Inhibitors For Cooling Water*

By HOBART SHIELDS, L. V. SORG and R. L. STUTZ

Introduction

INDUSTRIAL EXPANSION has caused a large increase in the demand for water. At the present time, the need in some areas can be met only by reuse. Because reuse of water greatly increases the possibility for scale deposition and corrosive attack, both industrial water users and vendors of water-conditioning agents have sought inhibitors that would materially retard these adverse effects.

Among the industrial users of water, the petroleum industry ranks near the top. For each barrel of crude oil processed, some 1,000 gallons of water pass through refinery equipment. Nearly all of this water is used for cooling and, hence, can be reused if cooling towers are provided.

In the Sugar Creek refinery of the Standard Oil Company, about 85 percent of the cooling-water needs are supplied from cooling towers. Consequently, a search for effective scale and corrosion inhibitors is of vital concern. Over the past nine years, about 50 inhibitors have been evaluated with techniques ranging from laboratory studies to refinery tests.

The refinery's cooling water is obtained from the Missouri River a few miles downstream from Kansas City and flows into the refinery units as shown in Figure 1. The total requirement is about 20 million gallons per day, of which 75 percent is used in box-type coolers. The water, after being freed of oil and contaminants, either returns to the river or is used to generate steam. A cold-flocculation water-clarification plant, which consists of a Dorr settler and two Spaulding precipitators, treats 3 to 4 million gallons per day as fresh water entering the cooling-tower system. The system serves a catalytic cracking unit, a vapor-recovery and polymerization plant, an alkylation plant, an Ultraformer, and a continuous crude-running and coking unit.

The required amount of cooling water varies from 75 to 100 million gallons per day. It is cooled in three induced-draft cooling towers having a total of 24 cells. Enough of the water is lost from the system through non-returnable uses to limit the cycles of concentration to 2.0 to 2.5, based upon sulfate content. Thus, not only the cost of protection is increased, but the use of any inhibitor that would unduly contaminate the refinery water-borne waste must be avoided because the non-returned water goes to the sewers.

Abstract

Corrosion inhibitors for refinery cooling water were subjected to four phases of testing: bench-scale, pilot plant, small size commercial cooling tower, and full plant-scale. Only three of the 50 inhibitors investigated in the past nine years were given full-scale trial. Of these, only the chromate type proved satisfactory in all phases of testing. Organic chromates were found to be particularly effective for the river water used in the refinery concerned. Phosphates, while exhibiting fair corrosion protection, had the disability of depositing scale, even at low pH values.

Tests were run for both carbon steel and Admiralty metal. Metal penetration rate and scale deposition data are given for specimens used in bench and pilot-plant tests in the presence of phosphate and chromate inhibitors. 5.8.1

The composition of the raw water, the fresh water to the cooling towers, and the recirculated water are shown in Table 1. A variable turbidity characterizes the river water; the changes are usually sudden. Water hardness is fairly high as is the sulfate content. The hardness reduction in the fresh water going to the cooling towers is incidental to the use of lime for clarification. The increase in sulfate content comes from the use of boiler-blowdown water to provide alkalinity for optimum performance of the flocculating agent. Subsequently, sulfuric acid is added to the clarified water to hold the cooling-tower water in the pH range of 8.0 to 8.3. No evidences of wood delignification have been observed in 10 years of operation at this pH level. The towers also have been treated against fungal attack. Sufficient inhibitor is also added to keep the desired level in the circulating water.

The water in the cooling towers is fairly hard and contains large amounts of sulfate and chloride. The numbers shown for inhibitor concentration are for total inhibitor as supplied by the vendor and not for any chemical radical.

Among the various inhibitors evaluated were:

1. Phosphates: simple structures, polyphosphates, combinations of polyphos-

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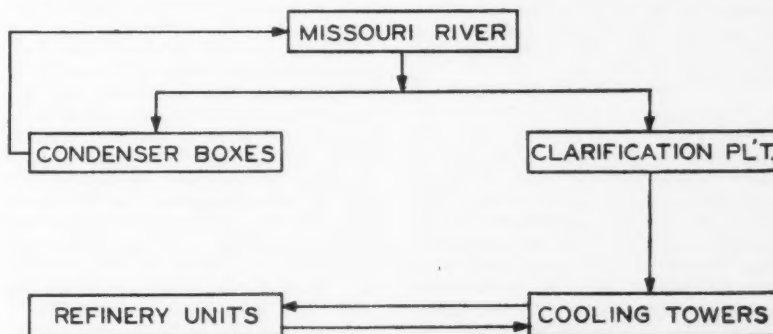
Figure 1—Refinery cooling water system.

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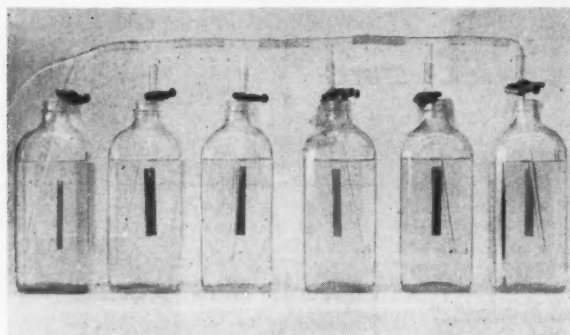
Figure 2—Bench scale test.
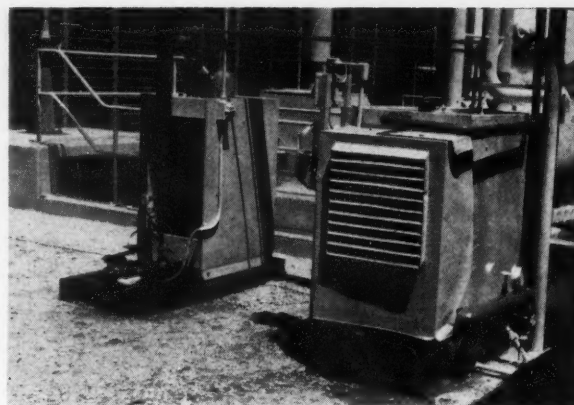
Figure 3—Pilot plant cooling towers.

TABLE 1—Composition of Cooling Waters*

	Raw	Fresh (Entering Cooling Towers)	Re-Circulated (Leaving Cooling Towers)
Turbidity	100-10,000	10	100
Hardness, Calcium, as CaCO₃	135	90	160
Hardness, Magnesium, as CaCO₃	95	65	130
Phenolphthalein Alkalinity, as CaCO₃	0	0	0
Methyl Orange Alkalinity, as CaCO₃	160	65	100
Sulfates, as Na₂SO₄	200	260	510
Chlorides, as NaCl	50	50	105
Silica, as SiO₂	15	...	...
Total Dissolved Solids	450	360	685
pH	7.9	7.2	8.2
Inhibitor	0	25	50

* Parts per million.

phates with promoters, and mixtures of polyphosphates with chromates; many were proprietary compounds.

2. Chromates: inorganic and several types of organic chromates, some proprietary and some specially synthesized.

3. Miscellaneous: ethylene diamine tetraacetic acid salts and modifications thereof, borates alone and in mixtures, zinc-promoted mixtures, and oils.

Procedure

The procedure used for selecting scale and corrosion inhibitors might be called "progressive elimination." The testing was divided into three phases. First, inhibitors were screened in the bench test. Those that showed promise were tried in pilot-plant runs, and the best ones were tested in the small commercial cooling tower. The few inhibitors that appeared economical and showed above-average protection against corrosion and scale in all three tests were tried subsequently in the refinery.

Test Specimens

Two kinds of metal test specimens were used in this work: a low-carbon steel representative of general piping and the tubing in some coolers, and Admiralty metal representative of the tubing in about 80 percent of the coolers. Two shapes of specimens were used: small strips that could be inserted into the mouth of a quart bottle, and closed-end cylinders that could be inserted into small glass-jacketed heat exchangers. The strips were used in the bench tests,

and the cylinders in the pilot-plant and small commercial cooling tower tests.

For bench tests, corrosion strips measuring 3 x ½ x 1/16 inches were cleaned thoroughly with steel wool and an abrasive cleaner. After being rinsed with distilled water, the strips were dried in an oven and weighed to the nearest 0.1 mg; then they were ready for suspension in the test solution.

The cylinders for use in the pilot-plant were machined from bar stock; they were open inside, closed at one end, and threaded at the other. The outside dimensions were 12x1⅜ inches. The specimens were weighed to 0.1 gram before and after the test, and also after they were cleaned free of scale. Colored photographs were taken of each cylinder after a test to provide a permanent record.

Bench Tests

The bench tests involved storage of the test strips in a tap-water solution of the inhibitors. Tap water was used because it is reasonably constant in composition and resembles refinery cooling water. Six test specimens were exposed separately at one time in solutions of different concentrations, as shown in Figure 2. The pH of the solution was adjusted initially to conform with the vendor's recommendations. Air was bubbled through the solutions to agitate them and keep them saturated with oxygen, as would be the case in a cooling tower. After seven days, the strips were withdrawn and the corrosion prod-

ucts were gently removed down to base metal with steel wool. After being dried, each strip was weighed to determine the metal loss. If the indicated corrosion rate was less than 0.01 inch per year, or if the strips looked particularly good upon visual inspection before cleaning, a pilot-plant test was run.

Pilot-Plant Tests

The pilot-plant tests represented the first attempt to approach a set of conditions of water composition and exposure close to actual plant operation. In the test, circulating water flowed through a small residential-size cooling tower, such as is used for home air-conditioning, and several simple heat exchangers in paralled flow. Each tower had a water capacity of 50 gallons. The pilot-plant towers are shown in Figure 3. Small size was important because of the flexibility and speed with which such important variables as water composition, conditions of exposure, and length of test could be changed.

Six heat exchangers of the type diagrammed in Figure 4, were used. Each consisted of a borosilicate glass jacket 2 inches in diameter and 1 foot long, with the cylindical specimen suspended inside. Water flowed through the annular space between the jacket and the cylinder. Steam passing at controlled rates through the inside of the test specimen heated the circulating water. Although temperature was partially adjusted by steam rate, water rate was controlling; it was set to simulate that in a refinery cooler.

One Admiralty and two steel specimens were exposed in each test. Water-outlet temperature from the units containing the Admiralty specimen and one steel specimen was regulated to 110 F; the other steel specimen was held at 120 F. Each test was run for one week, or longer if the specimen was still clean. At the end of the test, the specimens were removed, weighed, cleaned, and reweighed. From these data the corrosion rate and the amount of scale deposited were calculated.

Small-Tower Tests

The final step was testing of the most-effective inhibitors in the small com-
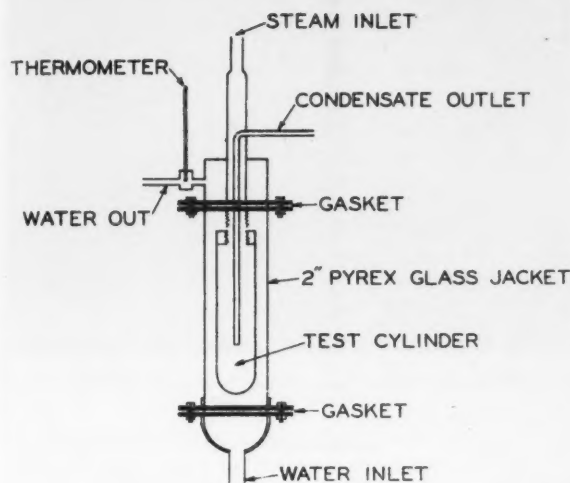
Figure 4—Pilot plant heat exchanger unit.
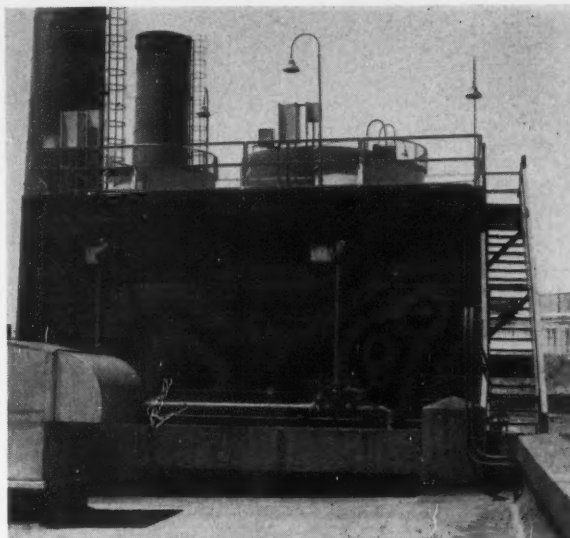
Figure 5—Small commercial cooling tower.

mercial tower shown in Figure 5. This structure was a two-cell induced-draft tower holding 8,000 gallons of steam condensate; it was designed to cool 1,000 gallons of the condensate per minute from 110 F to 85 F, with a wet-bulb temperature of 75 F. Makeup requirements were 200 gallons per minute. Two glass heat exchangers, identical with those at the pilot plants, were used with this system. The composition of the water, and other variables, were given the same close control as in the pilot-plant tests. Except for duration, which was two to four months, these tests were performed in the same manner as those in the pilot plant.

Results

In conditioning water for recycle use, the extension of data from experimental tests to plant operation is difficult. For reliability, extensive data are required.

The bench-scale tests were viewed mainly as a screening medium. For this reason not more than one set of data normally was obtained. Replication of results, as determined in developing the test, was good. Some typical data on identical runs were 33, 27 and 32 mils metal penetration per year. The validity of the bench test for screening was shown by correlation with the pilot-plant tests. No inhibitors that performed unsatisfactorily in the bench test passed the pilot-plant trial.

About 25 percent of the inhibitors screened were acceptable for pilot-plant examination. To obtain better data, multiple tests usually were performed on the more-promising agents. Typical results on a fortified phosphate were 23, 36, 31, and 36 mils of metal penetration per year. Hence, at this level more confidence can be placed in the quantitative values for scale and corrosion. Usually, such corrosion rates are greater than those obtained in a commercial plant because the pilot-plant conditions tend to

be slightly more severe. Also, in a good many tests these data were valued mainly for their qualitative characteristics. Scale laydown in the pilot plant at times exceeded that obtained in a plant trial so more significance was attached to corrosion data than to scale formation.

Data from the small commercial tower were viewed with reliance for corrosive attack but with less certainty for scale deposition. For example, three separate runs on an organic chromate gave 1, 2, and 1 mils of metal penetration per year, but no scale. Test run here gave an extremely good indication of performance in the plant. Since the unbuffered steam condensate in this system was extremely corrosive, a very severe test for effective performance was placed on an inhibitor. Only four inhibitors were tried in this tower.

Typical data on the tests with phosphates and chromates are shown in Table 2. These inhibitors also have been used in plant applications and may be compared later with that experience.

Simple phosphate inhibitors exhibit fair protection of iron but, in Missouri River water, scale was deposited at pH values as low as 6.0. Numerous analyses of the scale showed it always to be a combination of calcium, iron and phosphate. The exact molecular formula could not be determined.

Lignin-polyphosphate combinations also laid down a heavy scale that plugged the water annulus in the test exchanger. Hexametaphosphate combined with iron synergists operating at a pH of 5.8 to 6.2 deposited somewhat less scale. This scale, however, was exceedingly hard and could be removed only by scraping; chemical and X-ray analysis indicated it was a complex acid phosphate of iron and calcium.

Chromates gave the best protection at all levels studied. Both inorganic and organic chromates were evaluated. Inorganic chromates were immediately

recognized as excellent inhibitors for cooling water. However, handling hazards and a waste-disposal problem prevented use of these materials in this refinery.

Organic chromates are much less hazardous. Their molecular structure and lower chromium content are favorable. Also, they gave equivalent protection at much lower concentrations than the inorganic chromates. In addition to these advantages, the corrosion of iron in the presence of organic chromates was diffuse, usually appearing as streaks on the test specimens. Inorganic chromates, on the other hand, tended to produce pitting. Organic chromates were found to provide better protection if complemented with 2 ppm of $PO_4^=$ in the form of hexametaphosphate.

Plant Experience

Two phosphate combinations and one organic chromate were given full plant trial.

A lignin-polyphosphate combination was tried first. It was used without the benefit of the three-phase program just described. During a period of 1.5 years much difficulty was encountered with fouled coolers. Those that could be cleaned while in operation were reconditioned; others had to remain in operation until the unit was brought down. Upon opening coolers, extensive deposits of scale were found which increased in quantity in the hotter passes. Some tubes were so badly fouled that flow of water was almost impossible.

By this time, laboratory work on a hexametaphosphate was in progress. Pilot-plant tests indicated the laydown of a hard scale at the recommended pH values of 5.8 to 6.2, but corrosive attack was less. Because no other economical corrosion inhibitor had been found, and a change was necessary, the hexametaphosphate was given a plant trial.
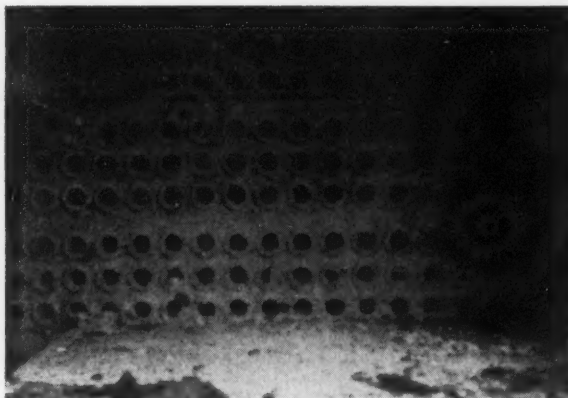
Figure 6—Exchanger surfaces after contact with water containing hexameta-phosphates for six months.
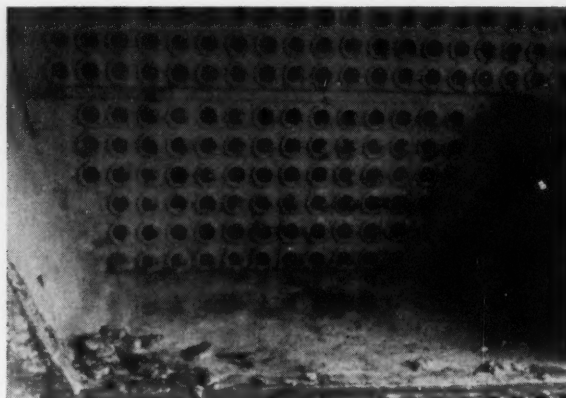
Figure 7—Exchanger surface after contact with water containing organic chromates for two years.

TABLE 2—Comparison of Test Results

	PHOSPHATES		CHROMATES		
	Bench	Pilot-Plant	Bench	Pilot-Plant	Small-Tower
No. of Tests............................	4	18	6	23	2
Metals Penetration, mils per year..........	1	29	2	4	1
Scale Deposition, grams per 1,000 gallons..	..	1.9	0.0	0.0	0.0

Operations soon showed the predictions of the pilot plant were correct. Scale deposition made it necessary to reduce throughput so that many of the critical coolers could be mechanically cleaned. Figure 6 shows the deposit of scale and some corrosion product from this operation. Some of the tubes were virtually closed with debris.

While much of the plant data on hexametaphosphates was being obtained, laboratory and pilot-plant investigations centered on organic chromates. In combination with a small amount of sodium hexametaphosphate, these compounds produced excellent corrosion protection and only film-like scale. Thus, after several months of operation, the inhibitor

was changed to an organic chromate complemented by 2 ppm of hexametaphosphate as PO_4^-.

The excellent protection afforded after two years of operation with this combination is shown in Figure 7. Optimum results were obtained in the pH range of 8.0 to 8.3. If the pH was lowered to 7.0 to 7.5, a powder-like sludge of calcium acid phosphate developed in large quantities which at times built up in front of cooler baffles. However, no sludge appeared when operations were in the optimum pH range. The operations were so successful that water cooling was never a problem.

The extensive tests on a plant scale showed the corrosion rate for the hexa-

metaphosphate to be 16 mils per year, as compared with the pilot-plant prediction of 29. Scale deposition was 1.0 gram per 1,000 gallons, compared with 1.9 predicted. For the organic chromate, metal penetration was 1 mil per year, as predicted in the small commercial tower. Scale deposits were negligible in many parts of the system.

Conclusion

Plant application of organic chromates has shown effective performance as expected from the investigational work. However, two weaknesses still persist: (1) The organic chromate is degraded and made ineffective if mercaptan-containing oil leaks into the water-circulation system. The mercaptans react with the chromium to precipitate chromium sulfide. Thus, excess amounts of costly organic chromate must be added to compensate for that deactivated. (2) The organic portion of the inhibitor, when disintegrated, is insoluble in water and collects as a gelatinious sludge on metal surfaces. The search continues for a corrosion and scale inhibitor that is effective under all circumstances.

Any discussion of this article not published above will appear in the December, 1959 issue

NATIONAL ASSOCIATION of CORROSION ENGINEERS

Summary of Questionnaire Replies On Corrosion in HF Alkylation Units*

A Report of NACE Task Group T-5A-6* On HF Corrosion

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Basic Objective

THE PURPOSE of this report is to help determine the nature and extent of corrosion problems in HF acid alkylation units in the petroleum industry. Task Group T-5A-6 hopes eventually to make possible the solving of these problems through cooperative effort in the industry and the utilization of any help that can be obtained from the users and manufacturers of hydrofluoric acid.

Introduction

The HF alkylation process operates by reacting an olefin, such as butylene, with isobutane to form saturated branched-chain hydrocarbons. Alkylate, the end product, has very high antiknock properties and is used in aviation gasoline and premium motor fuels.

The isobutane and the olefins are fed to a cooled contactor simultaneously with the introduction of hydrofluoric acid of 85 percent+ strength. The reaction takes place at a temperature below 100 F, with an excess of isobutane to prevent undesirable olefin-olefin reactions. After intimate contact in a reactor, the hydrocarbons are separated from the acid in a settler. Most of the separated acid is recycled to the contactor. However, some is purified of acid-soluble oils in a regenerator. Traces of hydrofluoric acid are removed from the hydrocarbons in the acid stripper. The hydrocarbons are then fractionated into the recycle isobutane, butane, and alkylate. Figure 1 shows a schematic diagram of a typical unit.

Since weak hydrofluoric acid is very corrosive to carbon steel, many items of equipment in a unit are subject to severe corrosion when water enters the system from leaks or is concentrated by distillation during operation. As a result, most of the corrosion problems encountered in HF alkylation units originate from this source.

Summary of Types of Corrosion

The corrosion problems, as reported in the replies to a questionnaire mailed to

the HF Industry, fall into the following basic categories:

1. Uniform Corrosion
2. Pitting
3. Grooving
4. Weld Decay
5. Hydrogen Attack
6. Stress Corrosion Cracking

Uniform Corrosion, Pitting, and Grooving

Uniform corrosion, pitting and grooving is confined largely to carbon steel in contact with substances other than the anhydrous acid. Such corrosion occurs usually during periods of abnormal operation when excess water gets into the system and forms weak acid in equipment designed for operation under anhydrous conditions. Aqueous HF attack on carbon steel can be very rapid.

This type of attack has been controlled largely by the use of inhibitors, neutralizers, and operating techniques that keep the water in the system at a low value at all times.

Pitting and grooving are special forms of general corrosion that the attack assumes under certain conditions.

General corrosion of Monel and nickel has been experienced in HF alkylation units in the presence of oxygen. This attack can be severe; in Monel, the nickel appears to be the component that is corroded in a preferential manner. Figure 2 shows the attack that occurred on a 16-gauge Monel evacuation stack lining from HF vapors and oxygen in less than two years' exposure. Figure 3 is a photomicrograph of the lining in which the nature of the attack is shown. This type of attack limits the use of Monel in HF alkylation units to equipment where oxygen is absent.

Weld Decay

Weld decay is reported on carbon steel weld metal exposed to both anhydrous and aqueous HF environments. In both cases, the attack is more severe on the weld deposit than on the base metal of a similar composition. High corrosion rates have been observed on carbon steel weld deposits exposed to anhydrous HF, where

Abstract

Corrosion in HF alkylation units is studied through a summary of replies to questionnaires mailed to HF industry representatives. The following types of corrosion are considered individually: uniform corrosion, pitting, grooving, weld decay, hydrogen attack, and stress corrosion cracking. Detailed accounts are given on corrosion occurring on component parts of contactors, acid settlers, acid stripper systems, acid regeneration systems, isobutane fractionating systems, debutanizer systems, depropanizer systems, tar systems and evacuation systems. Control measures used to mitigate corrosion are reported where available.

4.3.2

the attack on the wrought carbon steel was negligible.

The reason for this attack has not been established. However, it appears to be related to the crystalline structure of the metal.

Hydrogen Attack

Hydrogen attack in the form of embrittlement, fissuring, cracking and blistering has been observed in several items of equipment. Figure 4 shows small superficial hydrogen blisters in the interior of an acid stripper tower. The blisters average about ¼ inch by ⅛ inch, with a skin about 1/64 inch thick. Some of the blisters break open and the skin is corroded away, leaving shallow pits. The attack does not appear to be related either to acid strength or to temperature, as the attack has been reported in acid stripper towers at approximately 200 F, and in acid storage tanks at ambient temperatures.

One company reported the replacement of a tower due to hydrogen blisters. Failure of bolting in contactors was reported, as was hydrogen activity on acid settlers, storage tanks, and other equipment.

The mechanism of the attack has not been established, nor have control methods been devised other than the use of Monel or strip lining with carbon steel.

Stress Corrosion Cracking

Stress corrosion cracking was reported on both ferrous and nonferrous materials. Residual and applied stresses appear to be factors in the failures. A number of failures of hardened steel bolting were
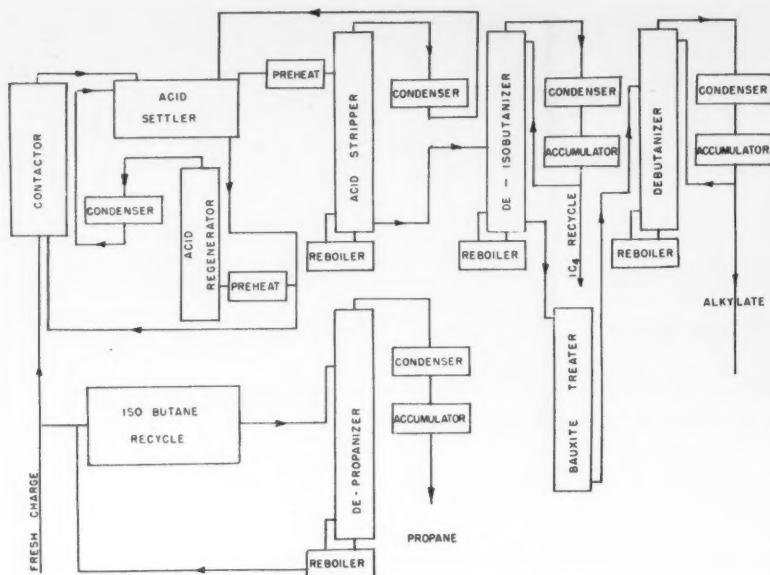
Figure 1—Schematic flow diagram of a typical HF alkylation unit.

Figure 2—Attack on Monel by HF acid vapors in the presence of oxygen.

reported. Mild steel bolting at a low applied stress appears to be superior to the hardened bolting. The failures are believed to be the result of hydrogen embrittlement.

Monel, which is resistant to stress corrosion cracking in the annealed condition, fails under high loads or when in the unannealed condition. The presence of oxygen accelerates stress cracking of Monel. In the absence of oxygen, Monel bolting performs satisfactorily if the applied stress is controlled by the use of a torque wrench. Duranickel is reported to be superior to Monel for bolting in HF service when oxygen is present.

Monel exchanger tubes have failed in HF service when not properly heat treated. Careful fabrication methods and the use of properly heat treated tubes will result in satisfactory performance. Figure 5 shows a Monel exchanger tube that failed from stress corrosion cracking in HF service. The tubes had not been stress relieved before installation. Figure 6 is a photomicrograph of the tube, which shows the intergranular nature of the major failures with numerous short transcrystalline cracks.

Summary of Questionnaire Results

Ten refineries, in response to a questionnaire, reported their corrosion experience in operating HF alkylation units. These results have been summarized in the report that follows. To facilitate the use of the information, each process function in a unit has been treated separately.

Contactors

Two refineries reported attack on carbon steel contactor shells, with pits $\frac{1}{4}$ inch in diameter by $\frac{1}{8}$ inch deep, and small hydrogen blisters 1 inch in diameter by $\frac{1}{4}$ inch high. No control measures were cited.

Another refinery reported general corrosion of the interior and exterior of the contactor cooling coil. A finned coil was replaced with a plain "U" tube coil, and water treatment inaugurated to control waterside corrosion of the coil. A third refinery reported breakage of carbon steel bolting material in the contactor. Mild carbon steel replacement bolting appears to give satisfactory service. Hydrogen blistering of internal baffles was reported by one refinery. Blisters were drilled to prevent further damage.

Acid Settler

One refinery reported general corrosion, pitting and blistering of the carbon steel shell of the acid settler, and the breakage of carbon steel (ASTM A-96, Class C) bolts. Repairs were made in kind. Another company reported shell corrosion (.006 ipy), and the cracking of carbon steel internal bolting. No remedial measures were reported. A storage tank in one refinery was found to be undergoing hydrogen attack; however, no blisters of significant size had occurred.

Acid Stripper System

Towers

The carbon steel shell weld seams and trays of an acid stripper tower showed general corrosion from the HF in the charge to the tower. Shell-metal loss was low. Repairs were made with weld metal deposits on weld seams. Trays were replaced with Monel, which is giving satisfactory service.

Another refinery reported similar, but more severe, corosion on an acid stripper tower. In this case, corrosion was controlled by strip-lining with Monel.

A third refinery reported general corrosive attack of shell and trays of a stripper tower with hydrogen blistering. Initial large blisters were drilled to vent hydrogen and prevent further damage. Eventually, attack was so severe that the tower was replaced after eleven years of service. Monel trays were installed and
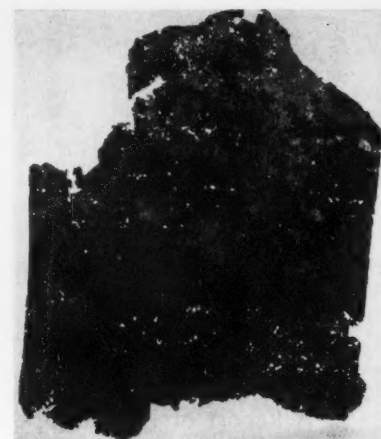
are giving excellent service. Hydrogen activity, as determined by a probe, is continuing. Promoter of the hydrogen attack has not been determined.

Exchangers

The carbon steel tubes and shell of the reboiler, on one unit operating at 200 F, showed a maximum corrosion rate of .01 ipy from a trace of HF in the hydrocarbon stream. In another unit, slight leakage in the tube rolls of an all carbon steel overhead condenser resulted in localized corrosion of the tubes. The use of a "U" type bundle with double tube sheets solved the problem.

Tanks

A carbon steel acid stripper feed drum containing hydrocarbon with .03 percent HF at 100 F showed weld attack, deep pits, and surface hydrogen blisters. The blisters disappeared when the blistered metal corroded away leaving shallow pits. Repairs were made by weld deposits over the corroded areas.

Acid Regeneration System

Towers

Six refineries reported severe corrosion (up to .250 ipy) on carbon steel regenerator towers. Four of the six refineries resorted to the use of a Monel clad tower and reported excellent results from its use. Slight etching of welds has been observed, with no observable attack on the Monel cladding. Two refineries continued to use carbon steel—one as solid metal, the other as a stress-relieved lining. Accelerated attack had been observed on field welds without stress relief.

Exchangers

In one refinery, stress corrosion cracking of Monel tubes in the overhead condenser was controlled by stress relief of the tubes.

Another refinery reported corrosion (0.2 ipy) on steel tubes and corrosion (.06 ipy) and blistering of the carbon steel shell. Satisfactory performance was obtained when Monel tubes and a Monel-clad shell were installed. The cracking of carbon steel (ASTM A-193-B-7) bolts
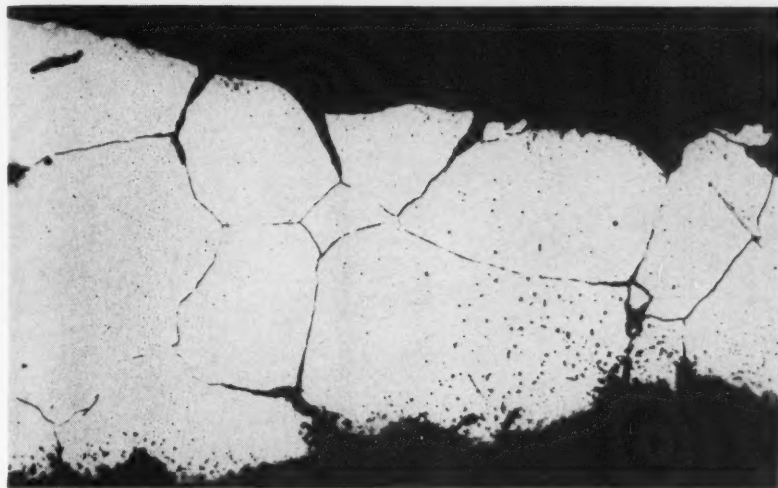
Figure 3—Photomicrograph of Monel sample shown in Figure 2. 250X, ferric chloride etch.
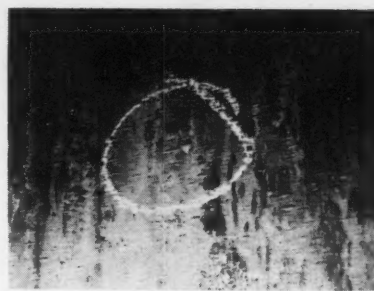
Figure 4—Hydrogen blisters on interior of acid stripper tower.

was reported by one company. Another refinery utilized carbon steel tubes in a double tube sheet, "U" tube bundle, to correct for local corrosion at the rolls. Corrosion rates of .005 ipy on tubes, and .025 ipy on the shell, were reported on the carbon steel "U" tubes and shell of a bottoms cooler.

Stress corrosion cracking of Monel tubes in a reboiler was controlled by stress relief of the Monel tubes at 1,000 F for one hour.

Corrosion at the welds (.10 ipy) of a double pipe preheater was reported. In another preheater bundle, carbon steel tubes corroded at .2 ipy and were replaced with Monel. Another refinery reported interior corrosion of preheater coils with a life of 245 days.

Lines

The carbon steel charge line to one regenerator tower corroded at .164 ipy and was replaced with Monel pipe. The same alloy was used to replace the carbon steel overhead vapor line which corroded at .14 ipy.

Bolting

Failure of carbon steel (ASTM A-193-B-7) bolting in acid areas was experienced in several refineries. Controlled torque on both carbon steel and K-Monel bolts was reported virtually to eliminate stress corrosion cracking. K-Monel bolts with a yield of 120,000 psi stressed to 60,000 psi had only 10 percent as many failures as carbon steel. The lowering of the loading on K-Monel to 45,000 psi is expected to eliminate all breakage of these bolts.

Isobutane Fractionating System

Towers

A grooving-type attack on the carbon steel shell of a fractionator operating at 240 F and 120 psi was controlled by careful operating during start-up periods to maintain system free of water.

In another unit, deep pitting (.275 inch in depth, by .5 inch in diameter) in a carbon steel bottom head on a tower op-

erating at 140 psi and 240 F bottom temperature was controlled by strip-lining of the head.

In a third unit, general corrosion (.02-.05 ipy) on the shell and trays of a tower operating at 100 psi and a 243 F bottom temperature was reported. No control measures have been used.

Exchangers

Isobutane fractionating tower overhead condensers showed dezincification of un-inhibited Admiralty tubes, corrosion of carbon steel tube sheets and carbon steel floating tube sheet cover, and preferential weld attack. The condenser operated at 98 psi and 132 F, with a trace of HF present. No control measures were reported.

In a second unit, general attack by weak HF on Admiralty tubes, and stress corrosion cracking of the (ASTM A-193-B-7) carbon steel bolts on the floating head were reported in both condenser and cooler. The condenser operated with an inlet temperature of 145 F and an outlet of 110 F, and cooler at 110 F inlet and 80 F outlet. Alternate bolts in the floating heads were replaced with K-Monel. Baffles were notched to prevent trapping of weak HF in the shell. Some failures of K-Monel bolts occurred in the cooler from stress corrosion cracking, probably from overstressing. In the same unit, stress corrosion cracking of carbon steel (ASTM A-193-B-7) bolts in the floating head of a recycle cooler, with general corrosion of tubes and tube sheets, was reported.

Piping

Corrosion (.042 ipy) was reported on carbon steel pipe in overhead vapor service at 128 F. Monel was used as a satisfactory replacement. The corrosion rate on piping carrying recycle isobutane was .014 ipy. Monel was used as replacement material.

Another refinery controlled corrosion in this piping by the use of an inhibitor injected into the line during the start-up period.

Tanks

A deisobutanizer tower overhead accumulator showed metal loss on shell, at welds, and on nozzles. General metal loss was .006 ipy and the weld attack much higher. Repairs were made by weld build-up.

Another refinery that reported the use of an inhibitor to control corrosion in the overhead vapor line stated that the inhibitor also controlled corrosion in the accumulator.

Recycle Storage Tanks

A recycle drum operating at 80 psi, 100 F with 300 ppm of HF, suffered attack on shell welds and on a nozzle at a rate of .012 ipy. Covering of the welds with a strip lining of carbon steel was the control measure used.

Corrosion in the lower portion of a recycle isobutane storage sphere was controlled by strip-lining the corroded area with carbon steel.

Debutanizer System

Towers

Corrosion of the carbon steel debutanizer tower shell and trays, at .04 ipy, was reported by one company. Carbon steel trays were replaced with Monel, and an inhibitor was used with caustic neutralization to reduce tower shell attack.

Another refinery reported that general mild corrosion of shell and trays was partially controlled by inhibitor injection, so that the rate was low enough that other corrective measures were not required.

Condensers

Corrosion of all carbon steel components of a debutanizer overhead condenser and stress corrosion cracking of carbon steel (ASTM A-193-B-7) bolting was reported. Attack was aggravated by occasional water leaks. The use of K-Monel bolts stopped the bolt breakage. Design changes, and the use of Muntz metal baffles, largely solved the other problems.

Another refinery reported corrosion of steel shells (maximum .25 ipy) and Admiralty tubes from ammonia used for neutralization. Corrosion of steel resulted from hydrolysis of silicon tetrafluoride from bauxite treater. Corrosion was reduced when soda ash was used for neutralization, and the bauxite treater recharged more frequently, reducing need for neutralization.

Vessels

The carbon steel shell and the internal piping of a debutanizer overhead accumu-
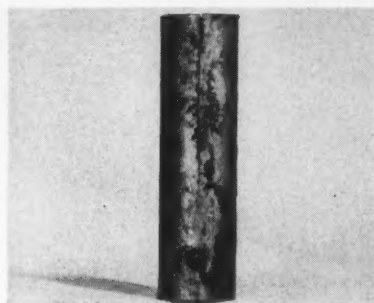
Figure 5—Stress corrosion crack of an unannealed Monel exchanger tube.

Figure 6—Photomicrograph of tube shown in Figure 5. 100X, unetched.

lator was attacked, with an average corrosion rate of .004 ipy, in one refinery.

Another refinery reported attack on the carbon steel shell of a similar vessel at a rate of .02 ipy. The use of activated alumina, instead of bauxite, in the defluorination treaters eliminated the formation of silicon tetrafluoride. The corrosion on the vessels occurred when the silicon tetrafluoride decomposed, releasing free HF.

Depropanizer System

General corrosion and weld decay was experienced in the depropanizer tower in one refinery. Welded bubble caps were replaced with a bolted type. General shell corrosion was not severe enough to justify remedial measures.

Another refinery reported general corrosion on depropanizer overhead condenser and stress corrosion of (ASTM A-193-B-7) carbon steel bolting. The general corrosion that occurred after bolt breakage permitted leaks. Satisfactory control was achieved by replacing every other bolt in the floating head flange with K-Monel.

Tar System

Attack on steam-jacketed tar lines and a tar storage tank was reported, with the attack apparently occurring in the vapor spaces. No corrosion control was used on the lines. However, a vent stack on the tank reduced corrosion.

Evacuation System

Piping

General corrosion was experienced on carbon steel pipe in most units. However, in general, the rates were low enough to justify the pipe's continued use.

Tanks

A nickel-clad caustic scrubber surge tank showed general corrosion in the vapor space by HF vapors and oxygen from air leakage. The tank operated under vacuum and contained weak caustic at 180 F, which was used as the neutralizing agent. Attack on the nickel cladding was controlled by redesigning the system to operate the tank without a vapor space.

Fume Dispersal Stacks

The lower portion of a carbon steel fume stack corroded severely, requiring frequent replacement. The installation of a reinforced polyester plastic liner in the lower portion of the stack has given satisfactory service.
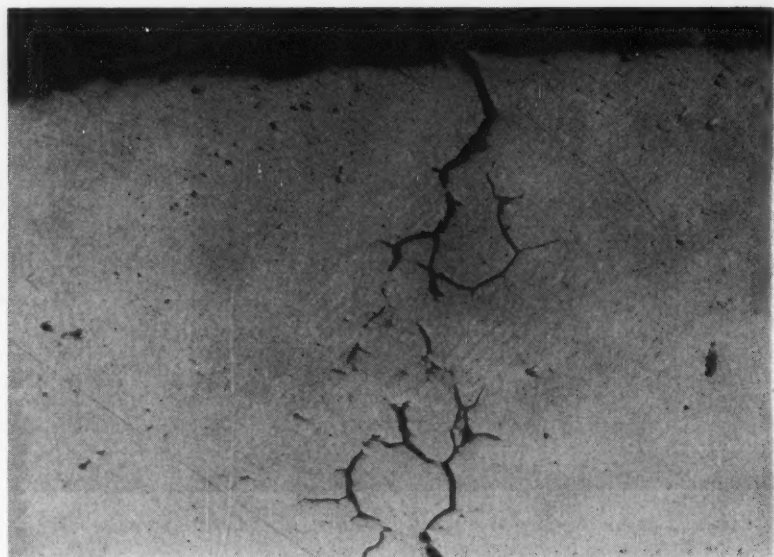
Another reported failure of a stack was from preferential weld attack at the seams. The use of seamless steel pipe and stress relief of the welded joining seams by peening was the control measure used.

Towers

A Monel-clad evacuation scrubber failed from corrosion by HF vapors and oxygen from air leaks. The clad tower was replaced with a heavy wall carbon steel vessel, and the scrubbing medium maintained alkaline at all times.

Another refinery reported weld seam attack and general corrosion on carbon steel in similar equipment. Redesign of the system has resulted in longer life.

A third refinery reported general corrosion of .015 ipy maximum, and preferential attack at the welds on a carbon steel tower in this service. No change in materials has been made.

General Findings

1. The use of a hydrofluoric acid detecting paint for use on lines and valves was reported.

2. Monel-trimmed gate valves were used in place of lubricated plug valves. The plug valves were unsatisfactory because corrosion products built up on the plug, resulting in operating difficulties.

3. Pump wear rings were removed, and the area built up with Monel weld deposit on both impeller and case. The weld deposits are machined, as wear rings, to give .018 inch clearance.

4. Monel has given satisfactory performance in mechanical pump seals.

5. Monel is used in bellows of Farris-type relief valves.

6. Monel-teflon, spiral-wound gaskets are used in exchangers.

7. Nordstrom hyperseal plug valves, with body overlay of Monel and plug overlay of Steelite No. 6 weld metal, were reported to give good service.

8. Mechanical damage to Monel exchanger tubes, such as occurs at edges of the woven wire sling used to support bundle when removing or installing in shell, will sometimes result in stress corrosion cracking.

9. Duranickel bolting was reported to be superior to other alloys for HF-contaminated atmospheric exposure.

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Corrosion Prevention in Tankers and Storage Tanks By Fogging or Flotation With an Inhibitor Solution*

By J. C. D. OOSTERHOUT, M. E. STANLEY and W. S. QUIMBY

Introduction

CONSIDERABLE ATTENTION has been given in recent years to tanker corrosion.[1,2,3,4] Cost figures on corrosion have been quoted[5] and various ways and means discussed for combatting this loss of steel. The reduction in corrosion in a practical and comparatively cheap manner is perhaps one of the few remaining avenues where a reduction in over-all tanker costs can be made. Most recent figures on corrosion losses as conservatively estimated by the API indicate a loss of approximately $150,000 per year for a T-2 type tanker in clean service. Considering that by a recent count there are 699 American tankers in service, the total loss is staggering.

Two general types of corrosion are found in tankers: (1) moderately uniform over-all rusting of the surfaces, and (2) localized pitting. The first type is encountered in both clean oil and crude oil tankers whereas the pitting type corrosion is more prevalent in crude oil tankers on horizontal surfaces. The most severe over-all rusting type corrosion generally occurs in the underdeck area where constant contact with moist air produces heavy attack.

Several methods of corrosion mitigation show promise. These include cargo inhibitors,[2] coatings,[6] cathodic protection[4] and flushing corrodable surfaces with a corrosion inhibitor solution.[6,7] Although all of these methods give significant protection, each has certain limitations and none is entirely satisfactory.

Most of the authors' work has been concentrated on the use of cargo inhibitors. This method gives nearly complete protection during the cargo leg of this voyage and the residual film of inhibitor remaining after unloading the cargo gives considerable protection during the return trip. The cargo inhibitor gives little protection to the underdeck area, however, because the tanks cannot be completely filled with cargo. Therefore, work was undertaken to find a technique for supplementing the protection being obtained with cargo inhibitors. Two techniques—flotation and fogging—have been found which show promise. These techniques both involve application to the exposed surfaces of the tanks of the same type inhibitor used for cargo inhibition. The inhibitor is applied during, or just prior to, the return voyage.

In the flotation method, a comparatively small amount (10-20 gallons) of

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inhibitor solution is dumped on the surface of the water as the tanks are being ballasted. The inhibitor floats on the water coating bulkheads and supporting members with a thin film of inhibitor as the tank fills. Ballast is then pressed into the top of the tank to cover the underdeck area with inhibitor. The ballast level is then adjusted as necessary to trim the ship. This method is similar to the flotation method described by Streed[8] but uses an inhibitor which will not degrade the next cargo and hence is not limited to use in cofferdam areas.

The fogging procedure consists of injecting a mixture of inhibitor solution and inert gas or steam into the tanks as a fine mist which condenses on all

Abstract

Two methods for reducing internal corrosion of tankers are described. These methods involve (1) flotation of an oil soluble inhibitor on ballast water to coat the internal surfaces of the tanks, and (2) fogging of inhibitor into empty tanks using an inert dispersant. Both methods were tested in the laboratory as well as in the field and were found to produce satisfactory results, particularly on underdeck surfaces. Data reported include effect of dry gas fogging versus wet gas fogging, effect of time in fogging oil soluble inhibitor with steam, and effect of oil soluble and water dispensable inhibitor on steel surfaces wetted with gasoline and/or sea water. 8.9.5

of the exposed surfaces in the tank. This is similar to the method described by Sudbury[7] but, because of the effectiveness of the inhibitor and the fine mist method of application, it is not necessary to collect and recirculate large volumes of inhibitor solution.

Laboratory Investigation

Flotation

Initial work on this procedure was carried out in a 4-ounce bottle containing a $\frac{1}{2}$ by 5 inch mild steel test coupon. The bottle with this coupon was slowly filled with water on the surface of which was deposited a thin film of inhibitor solution. Part of this solution was deposited on the metal; upon exposing the treated test coupon to sea water for seven days it was found that the layer of inhibitor on the metal had given satisfactory protection against rusting.

Following the preliminary work, the procedure of flotation was given a trial in a 300-barrel tank. The test coupons were suspended in the tank in various locations and water with inhibitor solution on the surface was slowly pumped into the tank. After the tank was filled, the test strips were removed and placed in synthetic sea water for seven days at 90 F. At the end of this time, the strips were removed, cleaned, and re-weighed. The results obtained in this manner are shown in Figure 1. In this figure, the inhibitor dosage is expressed in gallons per 9000 barrel ship's tank. However, in these laboratory experiments, the dosage was on an equivalent basis for a 300-barrel tank.

In view of the promising laboratory results, a field test was arranged. The data obtained from this test will be discussed later.

Fogging

Laboratory fogging experiments with air and steam as dispersants were carried out in small equipment and later in the 300-barrel tank mentioned previously and shown in Figure 2. Shown in this figure are the location of the test cou-
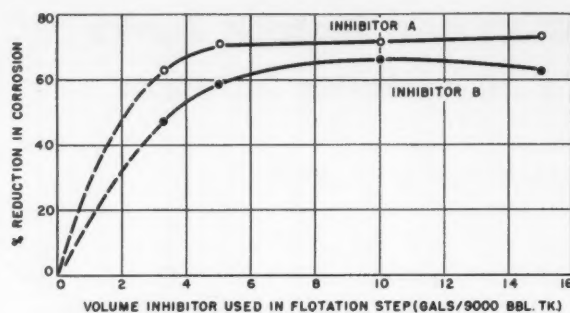
Figure 1—Relationship between volume of inhibitor used in flotation and percent reduction in corrosion in 7-day salt water exposure test.

Figure 2—Fogging in 300-barrel tank.

pons along the sides and at the top of the tank. Some of the test coupons are suspended in cans of which one side has been removed. This was done to simulate conditions in fogging behind beams and girders on the underdeck. Again inhibitor dosages were expressed on an equivalent basis for a 300-barrel tank.

Using the above procedure, investigations were made to evaluate:

a. Various inhibitors.

b. Various dispersants such as air, flue gas, and steam.

c. Varying injection times.

The data developed are presented in Tables 1 through 4, and it is indicated that:

(1) The larger inhibitor dosage of 10 gallons per 9000-barrel tank is superior to the smaller one tried (Table 1). In the actual field test, a dosage of 15 gallons was used.

(2) The oil soluble inhibitor studied is more effective than the water dispersible compound and both are superior to the other two tried (Table 2). The uninhibited test coupons, when wetted with sea water and partially immersed, usually rust more than the coupons totally immersed; therefore, with good inhibitor protection, the reduction in corrosion is greater as shown in Table 2.

(3) Fogging of the oil soluble inhibitor (Table 3) with steam produces about the same reduction in corrosion as fogging with air. The use of steam is preferred over air from the standpoint of the formation of explosive mixtures in the ship's tanks.

(4) A fogging time of 10 minutes (Table 4) is preferable to the longer periods. The shorter time for dispersing a given amount of inhibitor produces a denser fog and in turn a more effective film.

Data were also developed to determine the life of a once fogged surface upon subsequent exposure to gasoline and/or water as well as to establish the effect of surfaces wetted with water and/or gasoline on the deposition of the inhibitor film by fogging. The results obtained are shown in Tables 5 and 6.

Surfaces wetted with sea water and/or gasoline seem not to interfere too much with the action of the inhibitor solution.

The inhibitor film is not readily removed by subsequent contact with gasoline and/or sea water.

In view of the foregoing, fogging and flotation methods were field tested. The flotation field test was started one year ahead of the fogging test.

Flotation and Fogging Field Test

The flotation and fogging field test was carried out in a simple manner. The cargoes carried on the vessel concerned often contained a corrosion inhibitor. The flotation and fogging steps were added primarily to give protection on the underdeck areas.

Flotation

This procedure consisted of adding 16 gallons of inhibitor solution per 9000-barrel center tank or 8 gallons per 5000-barrel wing tank during the ballasting operations. Half of the inhibitor was added at the start of the operation and the other half when the tank was nearly full. The tank was then com-
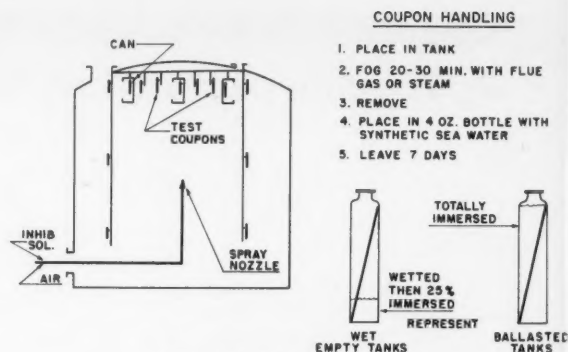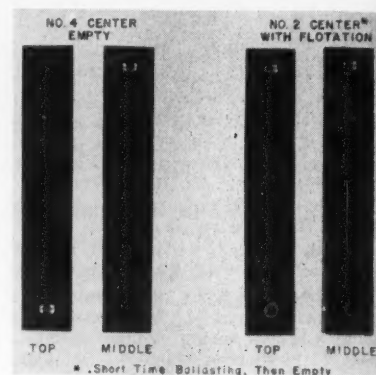
Figure 3—One-year steel test coupons from empty tanks.

pletely filled with water and the inhibitor was pressed against the underdeck. The inhibitor was added through the hatch by means of a 5-gallon bucket.

Flotation was tried in both normally ballasted tanks and normally empty

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TABLE 1—Effect of Inhibitor Dosage

SPECIMEN	Inhibitor Dosage, Gal/9000 Bbl Tank	Percent Reduction In Corrosion By Fogging* and 100% Immersion In Sea Water
Top Coupons	4.2 / 10	37 / 75
Middle Coupons	4.2 / 10	47 / 72
Bottom Coupons	4.2 / 10	42 / 69

* With Air.

TABLE 2—Fogging With Various Compounds Using Flue Gas as Dispersant

SPECIMEN	Test Conditions	PERCENT REDUCTION IN CORROSION WITH VARIOUS INHIBITORS			
		Oil Soluble	Oil & Water Insoluble	Water Soluble	Water Dispersable
Fogged Top Coupons	100% Immersion in Sea Water	72	22	38	70
Fogged Top Coupons Behind Baffles	100% Immersion in Sea Water	73	21	31	38
Fogged Side Coupons	100% Immersion in Sea Water	73	40	34	47
Non-Fogged, Dipped Coupons	100% Immersion in Sea Water	81	41	40	84
Fogged Top Coupons	Wetting & 25% Immersion	89	..	..	72
Non-Fogged, Dipped Coupons	Wetting & 25% Immersion	94	..	..	95

NO. 3 CENTER NO. FLOTATION — NO. 7 CENTER WITH FLOTATION

TOP MIDDLE TOP MIDDLE
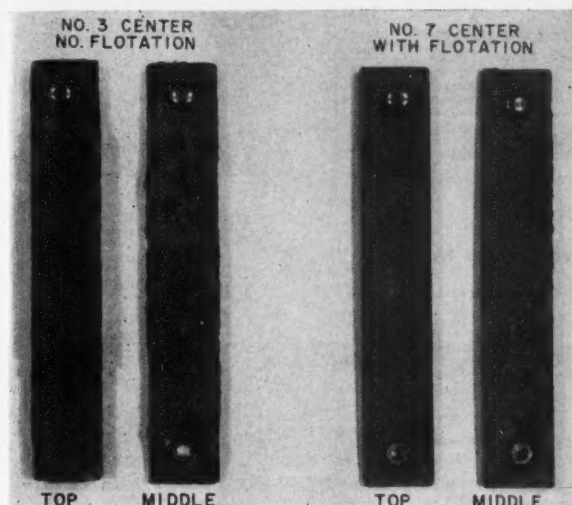
Figure 4—Two-year steel test coupons from ballasted tanks.

NO. 4 CENTER NO FOGGING — NO. 6 CENTER WITH FOGGING

TOP MIDDLE TOP MIDDLE
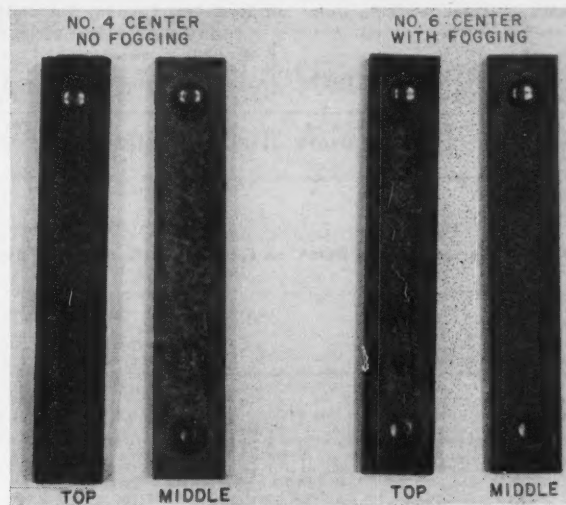
Figure 5—One-year steel test coupons from non-ballasted center tanks.

tanks. In the latter case, the tank was only temporarily filled with water to carry out the inhibitor contact. This required considerable pumping time.

Sand-blasted, weighed test coupons were suspended in various tanks near the underdeck and in the middle of the tanks. The results obtained are shown in Table 7. Additionally, Figures 3 and 4 show the extent of protection obtained by flotation.

The coupon results as well as the visual observations indicate that flotation reduces corrosion on the underdeck considerably, but does not significantly contribute to the reduction in corrosion of the bulkheads and bottom of the tanks already affected by the cargo inhibitor. A comparison of flotation and fogging will be shown later in this paper.

Fogging

The fogging operation in several tanks was simple. It consisted of turning on steam in the line leading to the nozzles; after displacement of any water of condensation from the line, the inhibitor solution was injected into the steam. The inhibitor was supplied from a vessel pressurized with air from the ship's compressor. Fifteen gallons of inhibitor solution were added to the center tank with the whole operation for one tank requiring about five to ten minutes.

The results of the one-year fogging test are summarized in Table 8. A picture of some of the test coupons examined is presented in Figure 5.

The data indicate that fogging reduces corrosion to a large extent on the underdeck and to some degree on the lower

surfaces. A comparison of flotation and fogging is shown in Table 9.

Fogging and flotation are about equal in effect for surfaces above the cargo level but the fogging is superior for surfaces below the cargo level.

The fogged inhibitor solution penetrates the rusty surfaces very well and practically stops further corrosion. This was found to be true with rusty test coupons which had been in the tank for one year when fogging was started.

In comparing the cost of the combination of fogging and flotation with available cost data[4] on the combination of anodes and inhibitor spraying, it appears that the fogging operation has the advantage. The cost of fogging and/or flotation per voyage approximates $400 as compared to approximately $800 for anodes and spraying.

Conclusions

Two new methods for reducing internal corrosion of tankers have been developed: (a) flotation of an oil soluble inhibitor on ballast water to coat the internal surfaces of the tanks, and (b) fogging of this same inhibitor into empty tanks using an inert dispersant.

These methods provide an economical technique for protecting the bulkheads and bottom of tanks during the ballast

TABLE 3—Comparison of Dry Gas Fogging Versus Wet Gas Fogging

Test Specimens	Percent Reduction In Corrosion By Fogging And 100% Immersion In Sea Water	
	Air Inhibitor Dispersant	Steam Inhibitor Dispersant
Top Coupons.........	82	72
Middle Coupons.......	74	76
Bottom Coupons......	72	73

TABLE 4—Effect of Time in Fogging Oil Soluble Inhibitor With Steam

Test Specimens	Percent Reduction In Corrosion By Fogging & 100% Immersion In Sea Water At Various Fogging Times		
	10 Minutes	20 Minutes	50 Minutes
Top Coupons......	72	62	64
Middle Coupons...	76	60	64
Bottoms Coupons..	73	50	58

TABLE 5—Effect of Oil Soluble and Water Dispersable Inhibitor on Steel Surfaces Wetted With Gasoline and/or Sea Water

Test Coupon Treatment	PERCENT REDUCTION IN CORROSION	
	Oil Soluble Inhibitor	Water Dispersable Inhibitor
1. Dipped in inhibitor, then wetted with sea water and partial immersion for one week......................................	92	90
2. Wetted with sea water, dipped in inhibitor, then wetted with sea water and 25 percent immersion for one week.....	70	88
3. Wetted with gasoline, dipped in inhibitor, then wetted with sea water and 25 percent immersion for one week........	92	84
4. Wetted with gasoline and sea water, then in inhibitor and then wetted with sea water and 25 percent immersion for one week..	95	85

TABLE 6—Results of Extended Fogging Test

Test Coupon Treatment	Test With Oil Soluble Inhibitor (Percent Reduction)
Fogged, wetted with sea water and 25% immersion for one week......	78
Fogged, then wetted with sea water and 25% immersion for one week and then one week in gasoline over sea water....................	79
Fogged, then wetted with sea water +25% immersion for one week, then one week in gasoline over sea water and then one week 25% immersion after wetting.............	70

TABLE 7—Corrosion Rate Data* on Steel Test Coupons Suspended in the Ship's Tanks

Location of Test Coupons	Normally Ballasted Tanks		Normally Empty Tanks	
	No. 3 Center; No Treatment	No. 7 Center; Flotation	No. 4 Center; No Treatment	No. 2 Center; Flotation
On Underdeck Frame...................	0.0133	0.0040	0.0123	0.0012
On Ladder At Top....................	0.0102	0.0025	......	......
On Bulkhead In Middle................	0.0053	0.0050	0.0028	0.0038

* In ipy.

TABLE 8—Corrosion Rate Data* on Fogged and Non-Fogged Steel Test Coupons From Ship's Tanks

Location of Coupons	NORMALLY EMPTY TANKS		
	No. 4 Center; No Treatment	No. 6 Center; With Fogging	No. 8 Center; With Fogging
On Underdeck................................	0.0123	0.0011	0.0041
On Ladder At Top...........................	......	0.0011	0.0021
On Bulkhead in Middle......................	0.0028	0.0024	0.0015

* In ipy.

or empty return voyage and, in addition, provide protection to the underdeck area which is not protected by use of anodes.

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3. A. B. Kurtz. Corrosion Control in Practice. *Trans. Soc. Naval Architects and Marine Engrs.*, 60, 382-441 (1952).
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8. E. R. Streed. Study of the Compatibility of the Floating Type Inhibitors and Cathodic Protection. *Corrosion*, 14, No. 3, 150t (1958) Mar.

DISCUSSION

Question by A. J. Freedman, Standard Oil Co. (Indiana), Whiting, Indiana: If this technique is applied to a refinery tank protection system, which technique is preferred—fogging or flotation—and what are the economics involved?

Reply by J. C. D. Oosterhout:
It is believed that in a refinery tank

Any discussion of this article not published above will appear in the December, 1959 issue

TABLE 9—Effectiveness of Fogging and Flotation

	Percent Reduction In Corrosion On Surfaces	
	Above Liquid Level	Below Liquid Level
With Fogging In:		
Tk. 6 vs. 4..............	91	14
Tk. 8 vs. 4..............	66	46
With Flotation In:		
Tk. 2 vs. 4..............	90	0
Tk. 7 vs. 3..............	76	6

protection system the fogging technique would be preferable. The economics involved in this particular instance will depend on various factors and no definite figures can be cited.

Question by K. L. Moore, Tidewater Oil Company, Delaware City, Delaware: Were the test coupons used in determining the inhibitor effectiveness clean or pre-rusted steel? If clean coupons were used for the reported data, were tests also made with pre-rusted coupons to see if the inhibitors would be equally as effective when used in typical rusted ship tanks?

Reply by J. C. D. Oosterhout:
The data reported pertain to cleaned test coupons; however, at the beginning of the field tests, rusty coupons from a previous test were present in the ship's tanks under test. Inhibitor fogging or flotation was found to be as effective with these rusty coupons as with cleaned specimens.

Study of Chemical Factors
Affecting Corrosion of Carbon Steel AISI 1020
By Liquid-Phase Fuming Nitric Acid*

By JOHN B. RITTENHOUSE* and DAVID M. MASON**
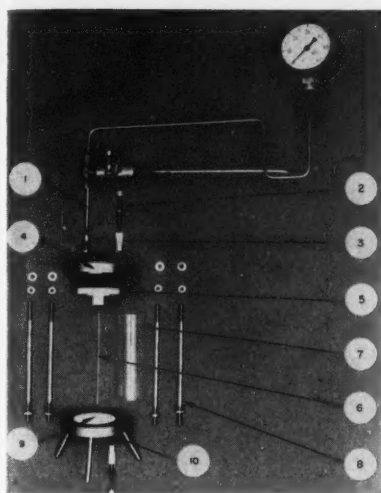
Figure 1—Electrical resistance cell. Legend: 1. Vent tube, 2. Electrical contacts, 3. Teflon seal and washer, 4. Top plate, 5. Top plate Teflon insert, 6. Sample tube, 7. Glass container tube (Kel-F lined), 8. Tie rods, 9. Bottom plate Teflon insert and 10. Bottom plate.
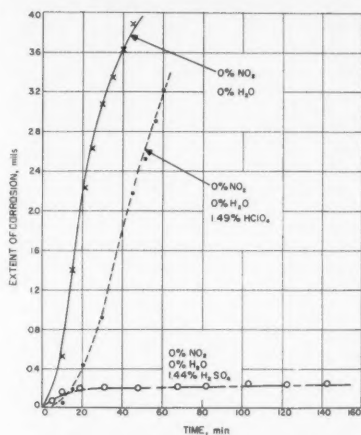
Figure 2—Effect of $HClO_4$ and H_2SO_4 in FNA on corrosion of AISI 1020 steel. Top curve is for 0 percent NO_2 and 0 percent H_2O; middle curve is for 0 percent NO_2, 0 percent H_2O and 1.49 percent $HClO_4$; bottom curve is for 0 percent NO_2, 0 percent H_2O and 1.44 percent H_2SO_4.
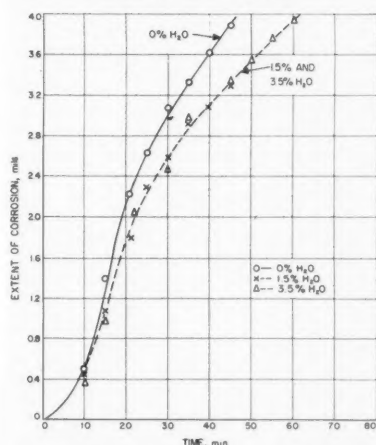
Figure 3—Effect of H_2O on corrosion of AISI 1020 in FNA (0 percent NO_2) at 130 F. Top curve is for 0 percent H_2O; bottom curve is for 1.5 percent and 3.5 percent H_2O.

Introduction

PREVIOUS INVESTIGATIONS[1,2,3] of the corrosive action of fuming nitric acid (FNA)[1] on several metals have shown that aluminum alloys and stainless steels containing chromium and nickel are relatively inert in either the liquid or vapor phases of FNA, stabilized with respect to thermal decomposition by the addition of 12 to 13 percent NO_2, 2 to 3 percent H_2O and with respect to corrosion by the addition of HF as an inhibitor. Aluminum alloys are used conventionally as storage containers for FNA, and stainless steel pressure vessels are used in missile systems.

It has been determined that steels of chromium content below 12 percent, such as plain carbon steels (i.e., AISI 1020), low-alloy steels containing approximately 1 percent chromium (i.e., AISI 4130) and low-chromium stainless steels (i.e., AISI 410) exhibited inconsistent passivation in FNA both with and without HF.[1] Reaction rates in the liquid phase of un-inhibited FNA were low (indicating borderline passivation) when a thin oxide film was present on the metal at the time of exposure. In the absence of the oxide film, reaction rates were high for these alloys, but they were also a function of the NO_2 and H_2O content of the FNA. The rates for these materials were usually higher in FNA containing HF, in both liquid and vapor phases, than in the FNA which did not contain HF. This latter behavior was not consistent with the findings for the chromium-nickel stainless steels or the aluminum alloys.

Purpose of this investigation was to study further the nature of corrosion of low-alloy steels in FNA and the manner in which the corrosion rates of plain carbon steel varied with NO_2 and H_2O concentrations. The plain carbon steel was selected because it is a relatively homogeneous, commercially available and widely used material which exhibits borderline passivity in FNA.

Corrosion studies usually are conducted by exposing coupons of the metal to the action of the corrosive for a definite period, and then computing the average corrosion rate during that time over the total area of the specimen from

(1) Throughout this paper, the term FNA is used to designate the ternary mixture HNO_3-NO_2-H_2O; all concentrations are expressed in weight percent.

Abstract

Corrosion rates of cold reduced and annealed plain carbon steel AISI 1020 tubing in fuming nitric acid (FNA) were obtained by measuring the change in electrical resistance of the tube with time. Corrosion rates decreased with increasing nitrogen dioxide (NO_2) concentration in FNA in the range 0 to 14 weight percent and also decreased with increasing H_2O content in the range 0 to 3.5 weight percent. This behavior indicates the possibility that nitronium ion (NO_2^+) or nitrogen pentoxide (N_2O_5) are involved in the rate-controlling step in the corrosion process.

Tentative or short-time passivation of the steel was obtained when the NO_2 concentration was greater than about 9 weight percent and H_2O concentration was 3.5 weight percent at the upper concentration range studied. Short-time passivation was also obtained when an oxide film formed under appropriate conditions was initially present on the specimen surface. Inhibition in the FNA media occurred only in those cases where the maximum rate of metal removal was less than 0.025 mil/min, corresponding to a weight of metal removed of approximately 0.1 mg/cm^2 of apparent surface. Adding 1.5 weight percent of either perchloric acid ($HClO_4$) or sulfuric acid (H_2SO_4), and 0.5 weight percent hydrofluoric acid (HF) produced inhibition in short-time experiments. 4.3.2

a determination of the sample's loss in weight. This method is satisfactory for long exposure periods and low rates, but it does not give information about the extent of corrosion in the earlier stages of attack during which the rates are believed to be high and the chemical role played by NO_2, H_2O, or HF on the corrosion process was to be studied. The initial stages of the reaction between the FNA and the metal are considered important for an understanding of the mechanism of the borderline passivity exhibited by the plain carbon steels.

Electrical Resistance Method of Corrosion Measurement

Continuous study of the earliest stages of the attack of FNA on plain carbon steels can be obtained by the measurement of the increase in resistance of a conductor resulting from the reduction of its cross sectional area as corrosion proceeds. This method has been used by several investigators.[4] For simplicity, a wire is ideal as the test section; however, greater sensitivity is obtained when a tube is used because small changes of cross section caused by chemical solution produce easily measurable changes of resistance.

Rate of chemical attack of the acid, with uniform dissolution of the external surface of the tube, can be expressed in mils of metal removed per unit time and evaluated in terms of the change of re-

TABLE 1—Nomenclature of Equations

D_f = final outer diameter of tube, in.
D_0 = original outer diameter of tube, in.
d = original inner diameter of tube, in.
n = valence of metal.
R = resistance of conductor, ohm.
R_f = measured resistance any time after initial resistance, corrected.
R_0 = initial measured resistance, corrected.
t = time.
w = extent of corrosion, inches.
M = any metal.

sistance of the material as shown in Equation 1 below:[2]

$$w = \frac{D_0 \pm \sqrt{D_0{}^2 - (D_0{}^2 - d^2)\left(1 - \frac{R_0}{R_f}\right)}}{2}$$

Chemistry and Corrosion of Metals in FNA Solutions

Corrosion of metals in FNA can be considered the result of several related chemical reactions. The equation representing the corrosion of a metal in nitric acid is shown below:

$$M + 2nHNO_3 \rightarrow M(NO_3)_n + nH_2O + nNO_2 \quad (2)$$
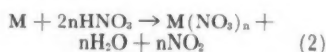
However, the kinetic mechanism of metal dissolution in FNA is more complicated than indicated by the simple chemical equation.

It has been postulated[5] that nitrogen dioxide can accept electrons from the metal and be reduced to nitrite ion as shown in a second corrosion reaction:

$$M + nNO_2 \rightarrow M(NO_2)_n \quad (3)$$

Then, in FNA the nitrite ion is oxidized to nitrogen dioxide as follows:

$$M(NO_2)_n + 2nHNO_3 \rightarrow 2nNO_2 + nH_2O + M(NO_3)_n \quad (4)$$

$$2M(NO_3)_n \rightarrow M_2O_n + 2nNO_2 + \frac{n}{2}O_2 \quad (5)$$
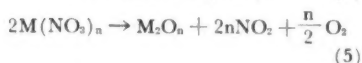
which results in the over-all corrosion reaction (Equation 2). In concentrated nitric acid, nitrogen dioxide undergoes 70 percent ionization[6, 7] in accordance with the reaction:[8, 9, 10]

$$2NO_2 \rightleftarrows N_2O_4 \rightleftarrows NO^+ + NO_3^- \quad (6)$$

It has also been reported[9] that NO_2^+ and NO_3^- are present in concentrated solutions of nitric acid:

$$N_2O_5 + H_2O \rightleftarrows 2HNO_3 \quad (7)$$

$$N_2O_5 \rightleftarrows NO_2^+ + NO_3^- \quad (8)$$

Subtracting Equation (8) from Equation (7) results in the equation of the self-ionization of nitric acid:

$$2HNO_3 \rightleftarrows NO_2^+ + NO_3^- + H_2O \quad (9)$$
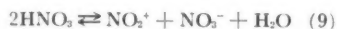
As seen from Equation (9), an increase of water in concentrated nitric acid reduces the NO_2^+ concentration.

Nitric acid is also known to undergo

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[2] Nomenclature is identified in Table 1.

association reactions with NO_3^- and H_2O.[11]

$$2HNO_3 + NO_3^- \rightleftarrows (HNO_3)_2\,NO_3^- \quad (10)$$

$$nHNO_3 + H_2O \rightleftarrows (HNO_3)_n\,H_2O \quad (11)$$
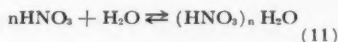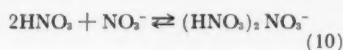
These equilibria have been directly investigated by Raman spectra and indirectly by other physical measurements.[2, 12, 14] Summing Equations (7) and (10),

$$N_2O_5 + NO_3^- + H_2O \rightleftarrows (HNO_3)_2\,NO_3^- \quad (12)$$
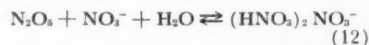
If equilibria (7) and (10) lie sufficiently to the right, then so will the Equation (12), and the addition of NO_3^- ions by the increase of NO_2 would tend to decrease the N_2O_5 concentration.

Ionization, according to the following reaction, will not be of significance in the present studies since it predominates as the water content is increased above 3 percent:

$$HNO_3 + H_2O \rightleftarrows H_3O^+ + NO_3^- \quad (13)$$
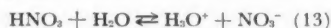
It also has been shown with Raman spectra[6] that proton donors stronger than HNO_3, such as sulfuric acid (H_2SO_4) and perchloric acid ($HClO_4$), when added to the FNA system donate a proton to form $H_2NO_3^+$, increasing the concentration of NO_2^+ ions and water, as shown in the following equation.[3]

$$H^+ + HNO_3 \rightleftarrows H_2NO_3^+ \rightleftarrows NO_2^+ + H_2O \quad (14)$$
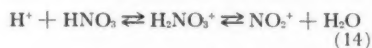
Thus the over-all effect of adding H_2SO_4 to HNO_3 is as follows:

$$HNO_3 + H_2SO_4 \rightleftarrows NO_2^+ + H_2O + HSO_4^- \quad (15)$$
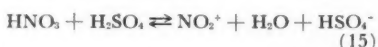
this reaction going appreciably to the right. Similarly for $HClO_4$:

$$HNO_3 + HClO_4 \rightleftarrows NO_2^+ + ClO_4^- + H_2O \quad (16)$$
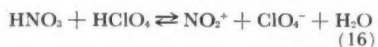
The effect of decreasing the species N_2O_5 when H_2SO_4 or $HClO_4$ are added to HNO_3 is shown by adding Equations (7) to (15) and (16) respectively:

$$N_2O_5 + H_2SO_4 \rightleftarrows NO_2^+ + HSO_4^- + HNO_3 \quad (17)$$

$$N_2O_5 + HClO_4 \rightleftarrows NO_2^+ + ClO_4^- + HNO_3 \quad (18)$$
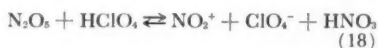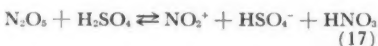
since the equilibria of Equations (7) and (8) lie to the right, so do the equilibria of Equations (17) and (18). Assuming that HSO_4^- or ClO_4^- ions have no specific influence on the corrosion rate, a change in corrosion rate in FNA, with either additive, would suggest that either the NO_2^+ or N_2O_5 is involved in the rate controlling step of the reaction.

The Results Section of this paper shows that the corrosion rates of the plain carbon steel AISI 1020, contain-

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[3] The ionic species $H_2NO_3^+$ can also be formed by the self dissociation of nitric acid as follows:

$$2HNO_3 \rightleftarrows H_2NO_3^+ + NO_3^- \quad (14a)$$

ing approximately 99 percent of the transition metal iron, decrease both with increasing nitrogen dioxide concentration and water concentration in FNA. This decrease in corrosion of the steel with increasing NO_2 concentration is in contrast with the behavior of aluminum alloys and stainless steels[2] in which the corrosion increased with increasing NO_2 content in FNA. The decrease in corrosion with increasing NO_2 with AISI 1020 is also opposite to the behavior of the transition metal titanium[15] in which the corrosion rates in anhydrous FNA increased with increasing NO_2 content. The corrosion rates of titanium, aluminum, and stainless steel decrease with increasing water concentration. It was suggested that in the case of titanium this behavior resulted from the rate determining role of both the nitrosonium (NO^+) and the nitronium (NO_2^+) ions. The nitrosonium ion was thought to be rate controlling in anhydrous FNA; whereas, the nitronium ion was considered to be rate controlling when the water concentration in the FNA was greater than 0.8 percent. Increasing the water concentration in FNA decreases the concentration of nitronium ion and N_2O_5 (Equation 9); also, an increase in H_2O decreases the corrosion rate of the AISI 1020 steel. This one experimental fact suggests that either N_2O_5 or nitronium ion may be involved in the rate-determining step.

The borderline passivity exhibited by iron in FNA not containing HF is believed to result from the formation of a thin film of iron oxides on the metal surface, whereas in FNA containing HF, passivation probably results from the formation of an oxy-fluoride coating on the metal surface. It has also been proposed[16] that in cases of large extent of corrosion the reduction in corrosion rate may result from the diluent effect of the corrosion products in the FNA, as shown in Equation (2).

Thermal Decomposition of FNA

When corrosion rates are low during long storage periods, thermal decomposition of FNA can change the concentration of the system as follows:[2]

$$4HNO_3 \rightleftarrows 4NO_2 + 2H_2O + O_2 \quad (19)$$

With increasing initial amounts of NO_2 and H_2O in the system, the equilibrium shown in Equation (19) is shifted to the left, thereby, effectively reducing the fraction of HNO_3 decomposed as well as the pressure from O_2 in a sealed container. In the present corrosion studies, for FNA compositions lean in H_2O or NO_2, the thermal decomposition reaction, Equation (19) will proceed together with the corrosion reaction, Equation (2).

Experimental Procedure

The electrical resistance cell used in these measurements is shown in Figure 1. The voltage drop across the specimen was measured at null galvanometer deflection with a Leeds and Northrup K-2 potentiometer. Current through the sample was determined by measuring the
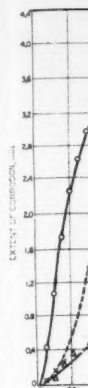
Figure 4—
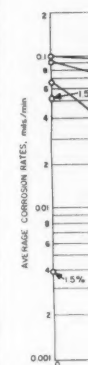
Figure 6—

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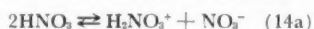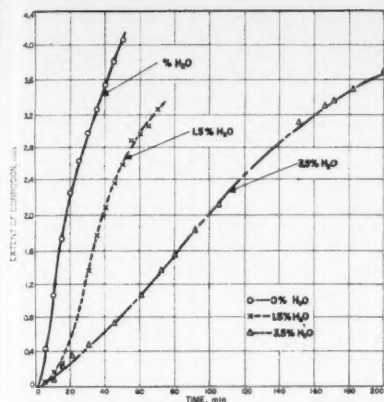
Figure 4—Effect of H₂O on corrosion of AISI 1020 in FNA (7 percent NO₂) at 130 F.
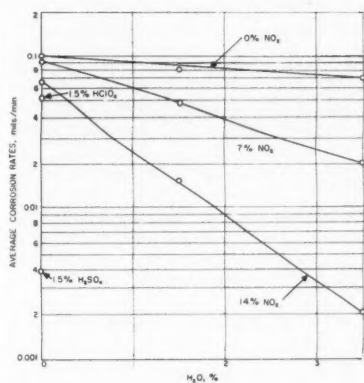
Figure 6—Average corrosion rates of AISI 1020 in FNA at 130 F.

Figure 5—Effect of H₂O on corrosion of AISI 1020 in FNA (14 percent NO₂) at 130 F.

voltage drop across a 1-ohm standard resistance in series with the specimen. The resistance of the specimen was calculated from Ohm's law.

Specimens used in the measurements were AISI 1020 cold reduced and annealed seamless tubing, 0.065-inch outer-diameter with 0.006-inch thick wall. According to ASTM specifications[II] for seamless tubing, the variation in outer diameter and concentricity is 0.004 inch and the wall thickness can be 22 percent larger but cannot be smaller than 0.006 inch. The tubes were approximately 4⅜ inches long, with about 80 percent of the length exposed to the action of the FNA in the cell. The spectrographic analysis of the tubing was carbon (C), 0.11; manganese (Mn) 0.45; silicon (Si), 0.21; phosphorus (P), 0.015; sulfur (S), 0.026 percent. Prior to exposure to the acid, each sample was identified, and the outer and inner diameters and length of each specimen were measured precisely.

The FNA used in these experiments was blended from pure nitric acid produced by vacuum distillation of a mixture of reagent-grade KNO₃ and H₂SO₄. The product was condensed at —79 C and stored at —30 C to minimize thermal decomposition; the HNO₃ thus pro-

duced was water-white at the storage temperature. Commercial NO₂ was fractionated and dried over P₂O₅.

Materials used in the studies of the effect of additives on the liquid-phase corrosion rates were prepared in the following manner: Anhydrous H₂SO₄ was made by mixing concentrated H₂SO₄ and SO₃ until acidimetric titration indicated that an excess of 0.005 weight fraction of SO₃ existed. Concentrated HClO₄, containing 30 percent H₂O, was mixed with an excess of H₂SO₄ and distilled. The product was titrated with standard sodium hydroxide (NaOH) solution and found to contain less than 0.6 percent H₂O.

To ascertain the effects of specimen preparation on the resulting corrosion rates, the following methods were employed: Before the start of a test, the steel specimen tube was sandblasted with 400-grit abrasive over the entire outer diameter of the tube, using nitrogen as the abrasive carrier. A blast of nitrogen without abrasive was used to remove any excess grit adhering to the metal, after which the tube was weighed. Prior to those experiments in which the tube was not sandblasted, the sample was degreased with warm detergent solution, followed by a rinse in cold water, hot water and acetone and then dried in a blast of nitrogen. Some samples were stored for seven days in a humid atmosphere, either after the degreasing operation or after the sandblasting operation.

At the beginning of an experiment, the electrical resistance of the circuit including the copper contacts but excluding the specimen, was measured at ambient temperature. The resistance of the contacts and specimen in place in the corrosion

cell was measured, blended nitric acid was introduced and at successive intervals resistance readings were taken and recorded with the entire assembly in a stirred constant-temperature water bath controlled to ±0.1 C.

A test was terminated by placing the cell in an ice bath, releasing the pressure in the cell, removing the acid and washing with three changes of distilled water. The corrosion cell was disassembled, the corroded length of the tube and the outer diameter were measured at the closest 0.001 inch and the sample was weighed.

Three corrections were applied to the resistance measurements: one for the resistance of the circuit exclusive of the sample, a correction for the increase in resistance of the test piece with increasing temperature of measurement and a correction for the resistance of the uncorroded portion of the tube. The extent of corrosion of the specimen at any time can be related to its change in resistance by Equation (1).

Results

Effect of Composition of FNA on Extent of Corrosion of AISI 1020 Steel

1. Presence of strong acid additives in FNA. Strong proton donors such as HClO₄ and H₂SO₄ added to HNO₃ should increase the NO₂⁺ concentration (as well as H₂O) and decrease N₂O₅. Corrosion of AISI 1020 steel in anhydrous HNO₃, with H₂SO₄ and HClO₄ added, is shown in Figure 2. As can be seen, 1.5 percent of either additive in HNO₃ decreases the rate of corrosion of the steel. Such behavior is compatible with N₂O₅ (but not NO₂⁺) being the rate determining species. However, the effect of the H₂SO₄ is so
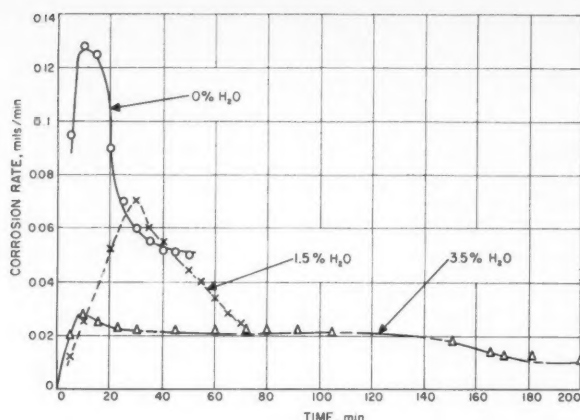
Figure 7—Instantaneous corrosion rates of AISI 1020 in FNA (7 percent NO₂) at 130 F.
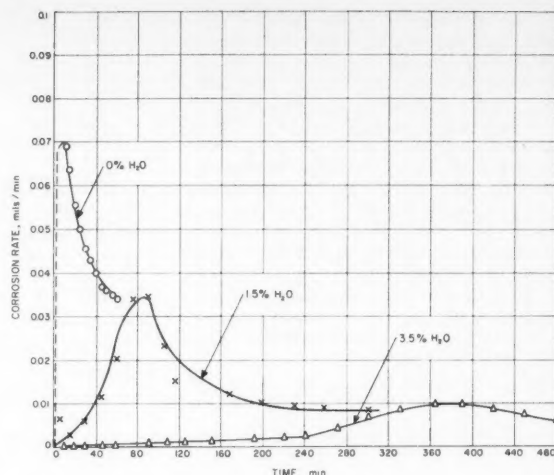
Figure 8—Instantaneous corrosion rates of AISI in FNA (14 percent NO₂) at 130 F.

marked that it is believed that some specific chemical effect of the additive may additionally retard the reaction. It is possible that specific chemical effects of both additives may completely overshadow the individual roles of NO_2^+ or N_2O_5.

2. Presence of water. In Figure 3, the effect of an increase in the H_2O concentration in FNA (0 percent NO_2) is shown to decrease the extent of corrosion.

The effect of 0 to 3.5 percent H_2O in FNA with 7 percent NO_2 in reducing the rate of corrosion of AISI 1020 steel is shown in Figure 4. Furthermore, it can be seen in Figure 5 that the retarding effect of H_2O on the extent of corrosion is enhanced when the concentration of the NO_2 is raised to 14 percent.

The average corrosion rates found by determining the average slope of the curves of Figures 3 through 5 decreased with increasing H_2O and NO_2 concentration as seen in Figure 6, a behavior which is consistent with NO_2^+ being the rate controlling ion because increasing H_2O and NO_2 concentrations decrease the concentration of NO_2^+.

Instantaneous corrosion rates obtained by numerical differentiation of the curves of Figures 3, 4 and 5 are shown in Figures 7 and 8. In most instances, the rates rise to a maximum and then decrease. The amount of metal removed was calculated at the maximum corrosion rate, and a rate of metal removal was thus determined.

At certain FNA concentrations, there are possibly two processes of metal corrosion acting simultaneously: metal removal and film formation. The metal solution process probably involves the oxidation of the iron by the NO_2^+ ions and formation of iron nitrates which are soluble in FNA. If the rate of metal removal is faster than the rate of film formation, the film does not have an opportunity to form, and passivation does not take place. Borderline passivity was exhibited when the rate of metal removal was near 0.03 mil/min while some degree of inhibition was indicated

with a rate of metal removal of 0.01 mil/min and a concentration of 14 percent NO_2 and 3.5 percent H_2O. This behavior shows that a critical rate of metal removal of less than 0.02 mil/min is required for passivation. Although passivation in the case of the addition of H_2SO_4 to anhydrous HNO_3 may have resulted from the specific chemical effects of the additive, the maximum rate reached in this case was 0.02 mil/min.

3. Presence of nitrogen dioxide. The effect of NO_2 concentration in FNA on the maximum corrosion rate of AISI 1020 steel is shown in Figure 9. Both the average rates and the maximum rates of corrosion as well as NO_2^+ and N_2O_5 concentrations, decrease with increasing NO_2 concentration in the FNA. It can be seen in Figure 9 that for an H_2O concentration of 3.5 percent the rate of metal removal falls below 0.03 mil/min when the NO_2 concentration approaches 9 percent. At FNA concentrations above 9 percent NO_2 (3.5 percent H_2O), tentative passivation will probably occur because the rate of metal removal falls below 0.025 mil/min. The effect of maximum rate on inhibition is summarized in Figure 10.

The competing mechanisms of metal solution and film formation may be controlled in the FNA by the regeneration or production at the metal surface of NO, which is rapidly converted to NO_2, and when produced at too rapid a rate, can actually disturb the film and hinder its formation. Rapid evolution of gas at the metal surface was actually observed with corrosion by anhydrous FNA of low NO_2 concentration. However, if the rate of metal removal is less than the rate of film formation, oxide films can be formed according to Equation (5). Therefore, at low rates of metal removal, passivation probably results from the formation of an oxide film; whereas, at high rates of metal removal, extensive corrosion is possible because the generation of gas at the metal surface prevents formation of tenacious impervious films,

and accelerated corrosion can proceed. Accelerated corrosion of steel in concentrated HNO_3 solutions has been reported by Evans[23] and in FNA by this Laboratory.[1] The possibility of surface phenomena such as chemisorption involving NO_2[18, 19, 20] should not be overlooked. It has been suggested that the excess NO_2 in concentrated (70 percent) HNO_3 may be chemisorbed on iron surfaces and cause tentative passivation.[21]

Effect of Preparation of Samples on Corrosion in FNA

In a prior investigation,[1] plain carbon steels and the iron based chromium alloy steels (AISI 4130, 410, 430, and 446) were observed to be inhibited by HF in FNA whenever the natural oxide film, which is formed in moist air, was present on the disk samples. When most of this film was disturbed by abrasion, corrosion of these metals was aggravated by the presence of HF in the FNA. This preliminary qualitative investigation indicated that the effectiveness of the film depended partly on the length of exposure of the freshly abraded sample to a humid atmosphere. The investigation indicated that approximately 3 days' exposure of the samples to a humid atmosphere will produce a partially protective film. The polished (to 400-grit abrasive paper) specimens were exposed to a humid atmosphere for 24 to 168 hours. Samples exposed in a humid atmosphere for 3 to 7 days exhibited a protective film which was effective for 16 hours in FNA (14 percent NO_2, 3.5 percent H_2O) at 130 F.

Figure 11 shows the effect of sample preparation on the extent of corrosion as determined by the electrical resistance measurement technique. The exact reason for the slight decrease in corrosion with the sandblasted tubular sample is not completely understood; however, a possible explanation could be that this behavior results from the increased surface area of the sample after grit blasting. The surface roughness of the samples were determined with a surface analyzer

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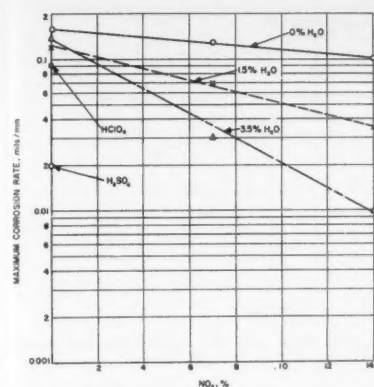
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Figure 9—Effect of NO₂ on maximum corrosion rate of AISI 1020 steel in FNA at 130 F.
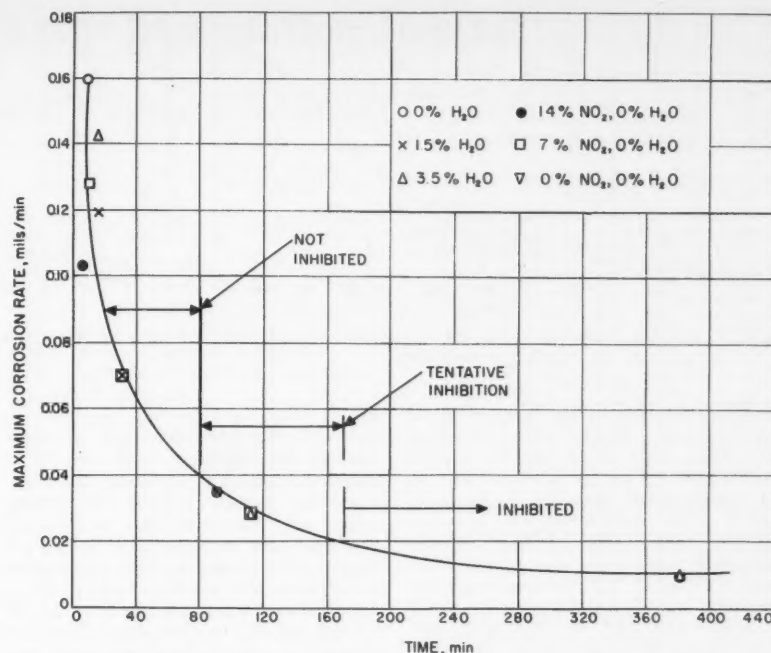
Figure 10—Effect of maximum corrosion rate on inhibition of AISI 1020 steel in FNA.

and found to be 3.5 microinches rms on the degreased sample, as compared to 6 microinches rms on the sandblasted tube. This difference in extent of corrosion between degreased and sandblasted specimens possibly results from statistical fluctuations of that data. The corrosion in FNA (14 percent NO₂, 1.5 percent H₂O) was reduced considerably with those tubular specimens that had received prior exposure for seven days to a humid atmosphere as can be seen in Figure 11. This behavior probably can be attributed to the protection afforded by an oxide film developed on the sample during the exposure to the humid atmosphere. Because of asperities on the sample surface, this film was probably not completely protective, as was indicated by the increase in the slope in the later stages of the corrosion-time curve. The maximum rate of metal removal by FNA for the sample which had been exposed to the humid atmosphere was below 0.01 mil/min, indicating that some passivation had occurred.

Effect of Temperature on Corrosion of AISI 1020 Steel in FNA

The increase in corrosion of AISI 1020 steel with increasing temperature is shown in Figure 12. The maximum corrosion rates were computed from the data, and an Arrhenius plot was obtained. The apparent activation energy calculated in this manner was 6.7 kcal, or approximately one half the value observed by Clark and Walsh.[22]

Effect of 0.5 Percent HF in FNA on Corrosion of AISI 1020 Steel

The anomalous behavior of plain carbon steels in the liquid and vapor phases of FNA was discussed in References 2 and 3. In Reference 16, it was shown that passivation of a chromium-nickel stainless steel in stabilized FNA (i.e., 14 percent NO₂, 3.5 percent H₂O, 0.5 percent HF) resulted from the formation *in situ* of a slightly soluble complex fluoride salt which formed a protective coating of metal oxy-fluoride on the surface. The extent of corrosion of the sandblasted AISI 1020 tubing in FNA (14 percent NO₂, 3.5 percent H₂O) without

HF, and also containing 0.5 percent HF, is shown in Figure 13. The maximum rate was computed for corrosion in the FNA containing HF and was found to be 0.013 mil/min, which is the range of maximum rates found previously to be critical for the production of passivation. Figure 13 shows that the corrosion-time curve for the FNA with HF is nearly horizontal after 30 minutes' exposure, indicating at least tentative passivation. The curve is rising slightly and the rate could possibly become higher with prolonged exposure periods.

One explanation for the high rates of corrosion previously observed with AISI 1020 in HF-stabilized FNA is that these early data were obtained by an intermittent weight-loss measurement which determined the average rate over a longer period of exposure than is represented by these experiments. These present studies, therefore, did not reproduce long-term exposure conditions during the latter portions of which the major corrosion damage could result. During the longer term storage of the samples in the previous investigations there was the possibility of cracks or voids forming in the protective film which could result in damage to the metal under the film and subsequent destruction of the protective nature of the coating. The present investigation includes only corrosion-rate measurements in the liquid phase, and it was observed in the previous studies[1] that the HF aggravated corrosion of low-carbon steel samples stored in the vapor space above HF-stabilized FNA.

When an oxide film, such as is produced by exposure to a humid atmosphere, was initially present on the samples, the passivation of plain carbon steel was virtually complete, during the short time tests involved, in FNA con-
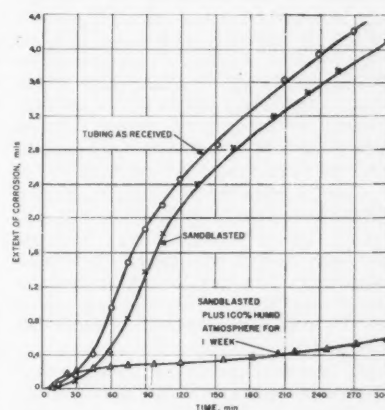
Figure 11—Effect of preparation of samples on corrosion of AISI 1020 in FNA (14 percent NO₂, 1.5 percent H₂O) at 130 F.

taining 14 percent NO₂, and 3.5 percent H₂O, with or without 0.5 percent HF. The nature of this oxide film is not completely understood at this time, nor have the conditions of its formation under controlled condition been investigated. Therefore, the use of plain carbon steel in stabilized FNA, with or without HF, is not recommended at the present time.

Conclusions

The corrosion rate of AISI 1020 steel in liquid-phase FNA decreases with increasing NO₂ and H₂O concentration. Since an increase in H₂O concentration decreases the concentration of NO₂ ions and N₂O₅ in FNA, the rate behavior with respect to changes in water concentration indicates that either of these species might enter the rate determining step of dissolution of the metal. An iron com-
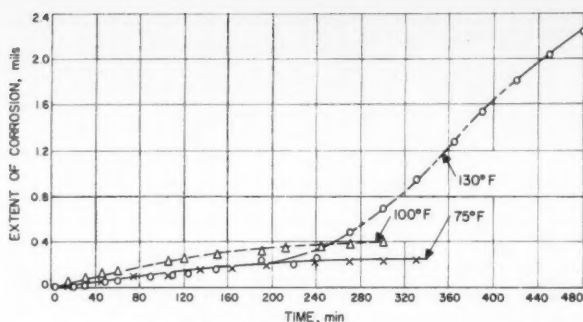
Figure 12—Corrosion of AISI 1020 in FNA (14 percent NO_2, 3.5 percent H_2O) as a function of temperature.
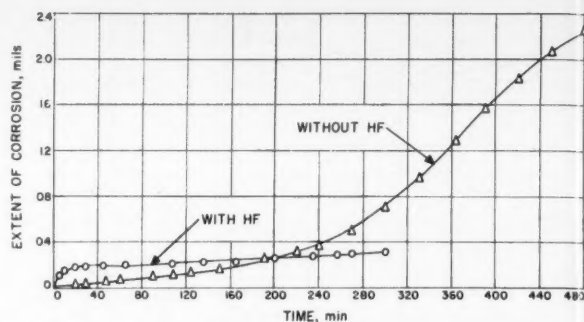
Figure 13—Effect of 0.5 percent HF in FNA (14 percent NO_2, 3.5 percent H_2O) on corrosion of AISI 1020 at 130 F.

pound conforming to the formula Fe_3O_4 was found as a residue in the corrosion cell. Thus, since Fe_3O_4 can be written $FeO \cdot Fe_2O_3$, or as $Fe(FeO_2)_2$[24] and is an intermediate between a ferrous and a ferric oxide spinel, a lower valence compound of iron in the metal-acid interface was a possibility. With increasing NO_2 concentration the corrosion rate goes down which is again consistent with NO_2^+ or N_2O_5 being rate determining. With increasing NO_2 concentrations in FNA, it is conceivable that NO_2 is chemisorbed on the iron surface, resulting in the formation of a protective adsorbed layer and the slowing down of the reaction rates, in keeping with the experimental evidence, it remains to be demonstrated experimentally that NO_2 is adsorbed on iron surfaces. An oxide layer formed by exposure of freshly cleaned iron surfaces to a humid atmosphere also induced borderline passivity in FNA.

The fact that the strong acid additives ($HClO_4$ and H_2SO_4) decrease the corrosion rates is in keeping with N_2O_5 but not with NO_2^+ being the rate determining species. However the additives themselves may have specific chemical effects resulting from the presence of HSO_4^- or ClO_4^- ions.[25]

It has been postulated in this paper that plain carbon steel can be tentatively passivated in FNA by three methods. First, short-time passivity is induced in FNA concentrations of 14 percent NO_2 and 3.5 percent H_2O. This passivation occurs, however, after considerable metal has been dissolved (Figure 5); hence, the inhibition is of theoretical but not of practical significance. Second, passivation can be produced if a thin oxide layer is initially present on the metal surface. These oxide layers have been produced experimentally by exposure of sandblasted or degreased samples to a humid atmosphere for periods from three to seven days. The method of controlled production of the oxide film, its nature and its thickness have not been studied in detail; hence, not enough is known of this passivation process, aside from

the short term tests of this investigation, for it to be considered a practical method. An imperfect oxide film or a semipermeable film resulting from uncontrolled deposition of the coating would offer no protection at all and would actually enhance the attack owing to the large cathodic film areas compared with the smaller anodic surface areas below the film imperfections. Third, 0.5 percent HF in FNA does inhibit the attack on plain carbon steels; however, previous long-term corrosion studies[2,3] have indicated that the passivation produced may be tentative. Furthermore, vapor phase corrosion of AISI 1020 was enhanced[2,3] by HF thus rendering additions of this compound unsuitable for inhibition in gas phase exposure of low carbon steels. Therefore, although it has been shown that passivation of AISI 1020 in FNA is possible, this material is not recommended for use with FNA of any concentration range.

Acknowledgments

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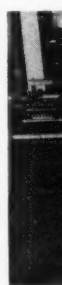
**Any discussion of this article not published above
will appear in the December, 1959 issue**

Photoelectric Information Selector*

By R. N. RIDE and P. J. KNUCKEY*

Introduction

DEFENSE STANDARDS Laboratories subscribed to the Corrosion Abstract Punch Card Service provided by the National Association of Corrosion Engineers. This service supplies approximately 2000 cards per year containing abstracted references in the field of corrosion and metal protection. Card edges are perforated for needle sorting. In order to reduce the time and to some extent the uncertainty involved in needling through large numbers of cards, an electronic-mechanical sorting system has been designed to select the data by an indirect method. A prototype machine has operated satisfactorily for more than a year.

This paper describes the principles of operation and the general layout of the selector and card punching machine. A general view of the equipment is shown in Figure 1.

A balance between construction simplicity and the cost of refinements to improve the sorting speed was necessary. This machine was not designed to be comparable in speed and function to the Rapid Selector[1] developed by the U. S. Departments of Commerce and Agriculture. This selector is both a sorting and photo-copying machine. Information abstracts and their appropriate "spot" code patterns are contained on 35mm film. The film is projected at the rate of 10,000 frames per minute and is scanned by a light beam and four photoelectric cells. The code pattern of a wanted abstract causes a blackout on the photoelectric cells. This signal triggers a high speed camera which photographs the wanted abstract frame directly on microfilm. The equipment described here operates on a similar principle but has been designed to perform the sorting operation only. Because design details are relatively simple, construction of the

equipment has required no special tools or facilities.

Where large volumes of data have to be handled by small libraries or laboratories, a photoelectric selector of this type (with an appropriately designed coding system) may be acceptable if the more expensive commercial equipment can not be justified.

General Description

The system is designed with the basic idea of selecting abstract card serial numbers without handling the cards themselves during selection. First, data on each abstract card is translated into numerical code groups which are registered as punched slots in a second series of cards known as Punch Cards. These are photographed on 16mm film in numerical sequence, thus forming an easily-handled memory from which information can be recovered by a sorting operation. Several important steps in film preparation are shown diagrammatically in Figure 2.

To extract information, a search card containing a punched code corresponding to the information required is placed in the selector. The film is scanned by a light beam and photoelectric cell, and all frames containing the required coding have their serial numbers stamped on a paper strip. These numbers are also those of the original abstract cards containing the information being sought. These cards can then be consulted directly.

Additional information can be stored in the system by simply coding and photographing punch cards and adding further lengths of film as required.

Details of System Components

Abstract Cards

The abstract cards as received are in random subject order and identified by

Abstract

Selector equipment has been developed to sort specific data on corrosion and metal protection topics from an extensive abstract reference library. The original data are coded and punched on cards which are photographed on 16mm film. In the selection operation, the film is scanned at 200 frames per minute by a light beam and photo-electric cell. Correspondence of code patterns with holes in a pre-punched search card "blacks out" the photo-electric cell and registers the serial number of the relevant reference on a paper strip.

The principles of operation, lay-out, advantages and limitations of a prototype machine are described.   2.4.4

a serial number. They contain the abstract information, author's name, journal reference and date of publication.

Coding

The field of corrosion and metal protection is divided into nine main headings and subdivided into more specific items. The coding system is a specially developed modification of the original NACE system.[2]

Technical matter is represented by random number 4-digit groups. Additional subdivisions of subject matter are represented by 3-letter groups.

Authors (one or two) can be accommodated by coding the first and third letters of surnames.

The journals are allocated numbers between 1 and 99 and are coded by the SF 7421 system.[2]

Publication date is classified according to whether the year of publication falls in the first five years (code letter A) or the second five years (code letter J) of the decade. These are further specified by the tens figure of the actual year, e.g. 1949 is 4J.

Punch Cards

These cards are used only in the preparation of the film. They are opaque 3

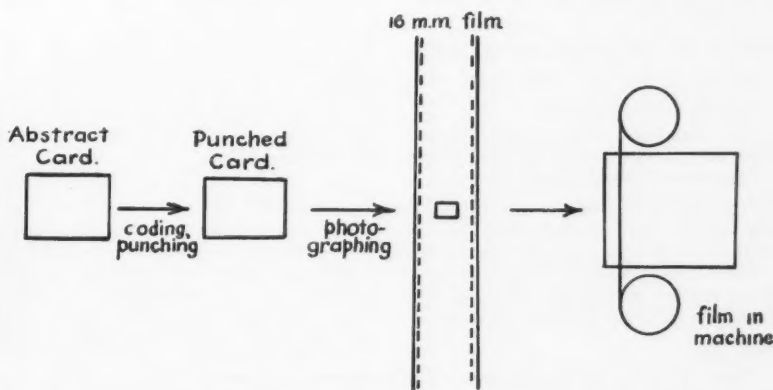Figure 1—General view of the selector, punching machine and card storage drawers.

Figure 2—Block diagram showing production of film.
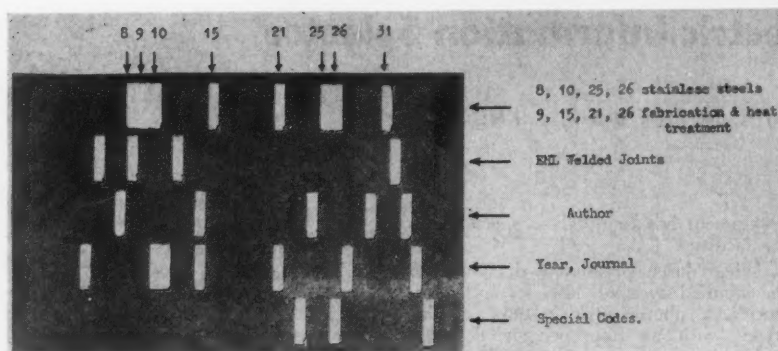
Figure 3—A typical punch card representing the codes of the abstract card.

Figure 4—Semi-automatic card punching machine.
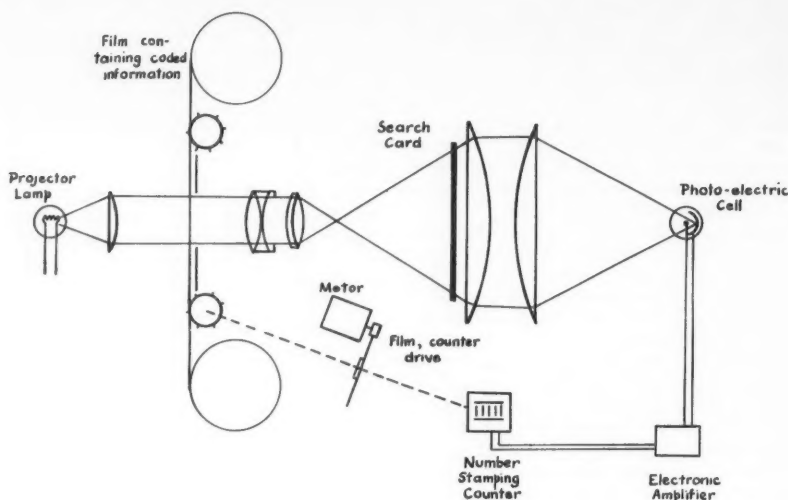
Figure 5—Schematic layout of photoelectric selector.

by 5-inch cards on which the coded contents of the appropriate abstract cards are punched in the form of $1/2$-inch x $1/8$-inch slots.

The cards are divided into five horizontal rows, each subdivided into 30 to 35 positions. The slot positions in each row correspond to code numbers or letters.

1st horizontal row deals with subject matter.

2nd horizontal row is a further subdivision of row 1.

3rd horizontal row deals with author(s).

4th horizontal row deals with year, journal.

5th horizontal row contains special codes for indicating "Book," "Symposium," "Trade Name" etc.

At the end of each row a special marker slot ensures correct registration and discrimination between rows during sorting.

Each Punch Card is given the same serial number as its parent abstract card. A typical example is shown in Figure 3.

Punching

Code slots in the punch cards and search cards are formed in a semi-auto-matic pneumatic punching machine (see Figure 4). A blank card is placed in a traversing card holder, the appropriate row code is set up on a keyboard and the punching commenced. The depressed keys arrest the travel of the card holder at the correct position for a slot to be punched. Once started, operation is controlled by a motor-driven camshaft operating the card movement and punching mechanisms in sequence till the end of the row is reached. The carriage is then returned automatically to the zero position. The keyboard is cleared, the codes for the next row are set up and the operation repeated. Multinumbering of the keys allows all six sets of codes to be accommodated on the one keyboard (35 keys). Average time of punching is one minute per card.

Photographing

The punch cards are photographed in serial number sequence on 100-foot lengths of 16mm film. A rigid optical bench-type set-up ensures accurate alignment of images on the film for batches photographed at different times. Automatic film movement is interlocked with shutter movement and card holder to ensure single exposures.
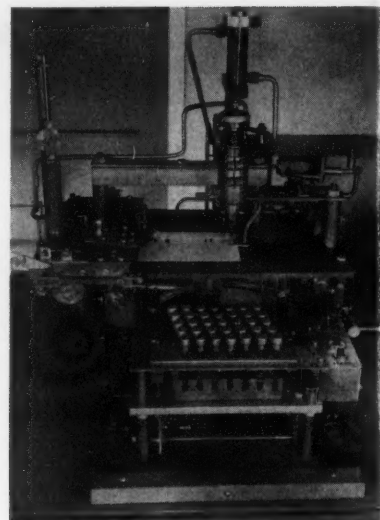
Sorting Machine

Schematic layout of the unit is shown in Figure 5; Figures 6 and 7 show detailed views. The film is used as a negative. Coded information appears as a pattern of black rectangular spots which are projected on a search card by a conventional projector optical system, the projected image being enlarged to the size of the original punch card. The film is driven in a continuous motion by an electric motor and positive sprocket drive. The coding spots appear as rows of shadows moving over the search card so that all Punch Card images contained in the film are, in effect, compared with the search card. Any light passing through the Search Card holes is focussed by a large condenser lens onto a photo-electric cell.

When a frame containing the required code momentarily covers all search slots by the projected shadows, no light strikes the photoelectric cell, causing a pulse to be transmitted to the amplifier. When the code required is not duplicated completely by the projected images, at least one slot on the search card is illuminated, so that light passes through to the photoelectric cell. Under this condition there is no registration.

Activation of the amplifier by a coincidence operates a number stamping counter (Figures 6 and 7). Pre-set at the beginning of each search operation, the counter is interlocked with the film drive to count the serial number of each frame as it is projected.

The amplified coincidence pulse operates a relay and chopper bar which prints a carbon paper impression of the coincidence serial number from the counter onto a paper strip. An automatic paper feed operates only after each registration.

Thus, the selector produces a strip of paper on which serial numbers are stamped of all frames on the film containing the code combination of the search card. These numbers are also, of course, the serial numbers of the corre-

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Figure 6—Projection lamp compartment showing lamp (center bottom), condenser lens (center), chopper bar relay (left) and mechanical links to numbering unit (right).

Figure 7—Front covers removed from amplifier and projection compartments. The film drive gear and projection lens are beneath the film reel. To the right is the search card in its holder. The numbering unit and paper drive rollers are mounted on the front of the projection lamp compartment (left). The extreme right compartment contains the photoelectric cell.

sponding original abstract cards. Because of optical system limitations in the present prototype machine, a certain amount of background light reaches the photoelectric cell in the total light extinction condition. This necessitates using a constant number of slots (13) in the search card to maintain a constant background level. When less than 13 significant slots are needed for a search, the balance to 13 is made up by punching special no-code slots in the search card. Every punch card contains eight no-code slots for use on these occasions. The amplifier is adjusted to discriminate between the constant background and the extra light reaching the photoelectric cell when one slot is illuminated.

Normal Search Operation

A search card, the same size as a Punch Card, is punched with the code of the desired information and inserted in the selector when normal search operation is to be performed. The counter is set at the starting number, using a count-down guide which is incorporated in the film for this purpose. The selector is started and the film allowed to run unattended.

At the end of the film, a shut-off is used to stop the film drive motor. A length of fully-exposed film generates a long black-out pulse from the photoelectric cell which activates a valve and relay circuit to interrupt the film drive motor power supply.

The paper strip containing the serial numbers of the appropriate frames is then used to select the abstract cards directly. The original abstract cards are actually handled only at this last stage of the search.

Performance and Characteristics

This selector scans at 200 frames per minute. Thus the film presently in use, containing approximately 7000 references, can be scanned in ¾ hour. Though slow
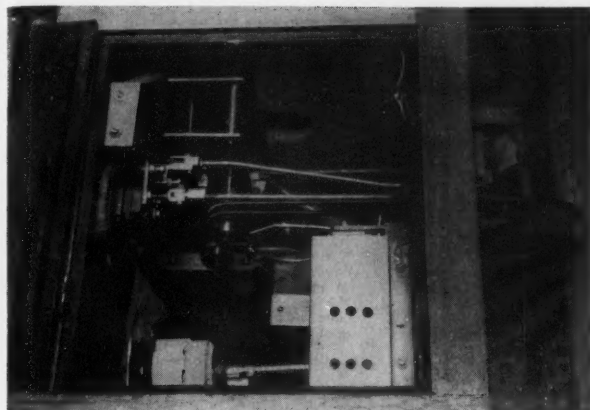
in comparison with some commercial card handling equipment, this speed is adequate for present requirements, especially as a normal library search covering the same number of sources and references could easily require several days. Approximately 16,000 references can be accommodated on a standard 400-foot reel.

The system as a whole can be adapted to several types of required data. The most frequent search is for information on a specific topic (rows 1 and 2). However, a particular line on each film frame may be selected for comparison with the search card, and it is therefore possible to search via the author's name, the year or journal. This allows a general search to be carried out: e.g., all articles by one author can be withdrawn.

During normal searches a number of spurious responses occur in addition to the authentic registrations. These are influenced by the following factors:

1. The required code combination may not be included specifically in the coding of a particular abstract card but may be occasionally present due to chance combinations from other code groups.

2. The greater the number of significant holes used in the search card (up to 13 maximum) the less is the probability of coincidence due to chance permutations.

3. Average optical density of a frame has some slight influence on the background light level. Occasionally, when a projected code pattern covers all but one search card hole, a spurious registration may occur if the background light level is abnormally low. This condition exists for heavily coded frames for which the total light transmission is lower than usual.

When specific searches are performed, between 5 and 10 percent of all cards sorted may be spurious registrations. The proportion is higher when a broad search

is undertaken. Spurious responses are recognized quickly when the abstract cards are consulted and cause little delay.

Main feature of the selector is that, with correct amplifier sensitivity, all cards containing a particular code will be selected. Any sorting irregularities do not result in wanted cards being ignored but rather the inclusion of irrelevant cards which can be readily rejected later.

General Advantages

General advantages of this machine system can be summarized as follows:

1. The system is more rapid and extensive than a library search.

2. The operating mechanisms are relatively simple compared with more expensive commercial equipment.

3. The search may be broad or specific according to the searcher's needs.

4. All relevant cards are selected.

5. Up to nine separate subjects may be accommodated on a single punch card, thus minimizing the need for cross references.

6. Though trained personnel are required to code the original abstract cards and preferably to select codes for searching, all other operations including punching of cards and the searching operation can be performed by unskilled persons.

7. Once the selector is set up and the search card is in position, the machine will operate unattended.

Acknowledgments

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Any discussion of this article not published above will appear in the December, 1959 issue

Classification of Topics Relating to Corrosion*

By MISS D. M. BRASHER*

Introduction

THE NEED for a comprehensive classification system for topics relating to corrosion became apparent when the Corrosion Group of the Chemical Research Laboratory, Teddington, England, decided to record and classify by subject matter the technical enquiries received.

An alphabetical arrangement of topics under four main subject divisions was considered unsuitable because it was desired to keep related topics together. A system was decided on to classify corrosion topics that would be useful for continuation of the corrosion bibliography and also for compiling a record of the advisory services. A fully classified system has the advantage over an alphabetical scheme of being independent of language; any specific subject in whatever language it is described should be found under the same number in a classified system.

Choice of a Basic System

The National Association of Corrosion Engineers Abstract Filing Index,[1] published in its final revised form in 1952, was suitable as a basis for the proposed classification. An alternate classification, the Universal Decimal Classification,[2] was considered unsuitable. This classification is now used widely for classification of scientific material, and, where possible, it is certainly desirable that subsidiary classification schemes should fit into this wider framework. It has been adopted and expanded to include the classification of metallurgical topics[3] although an alternate classification for use with punched cards has been issued by the American Society for Metals in conjunction with Special Libraries Association.[4]

Classification Problems

In the classification of corrosion topics, however, special difficulties arise.

The Universal Decimal Classification covers all branches of human thought and knowledge with no bias or special viewpoint. Section 620.19 in the Fifth International Edition of UDC[5] is entitled "Maladies des Matériaux. Influences et actions chimiques et physico-chimiques. Corrosion. Erosion."** Under this main heading, subject headings cover theories and types of corrosion, environmental, physical and chemical influences, methods of protection and testing. No provi-

sion is made for the metal, material, type of structure or equipment that is deteriorating (or for which protection is required), nor for the problems of corrosion in various industries. The subject of coatings is inadequately treated and requires subdivision according to type of coating.

These subjects, however, are covered elsewhere in the UDC and entries possibly could be placed accordingly; alternatively, they could be placed under 620.19 and connected by a colon to these related aspects as necessary. The first of these alternatives scatters the topics in a somewhat unsatisfactory manner. The second cannot be done as the system stands: there is no place, for example, for general corrosion of a specific metal or structure or for corrosion in a specific industry.

For the laboratory's purpose, a classification of all topics relating to corrosion, approached from a corrosion viewpoint, was considered desirable.

W. H. J. Vernon in his book[6] classified corrosion topics into four sections, which he described as follows:

I. General: Various types of corrosion; factors influencing the corrosion process.

II. Corroding Medium.

III. The Metal, Alloy, or Manufactured Article, etc., undergoing or resisting Corrosion.

IV. Methods of Protection.

Systematic classification was not carried further than this; under each of these headings subjects appeared in alphabetical order. This arrangement was continued in the Chemical Research Laboratory Card-Index Corrosion Bibliography maintained from 1928 to 1950.

The NACE system has a basic division into eight main headings: 1. General, 2. Testing, 3. Characteristic Corrosion Phenomena, 4. Corrosive Environments, 5. Preventive Measures, 6. Materials of Construction, 7. Equipment, and 8. Industries.

Though fully classified, this system was not considered sufficiently detailed. Less detailed classification is required when the system is used with punched cards (as is done with the NACE Abstract Cards), but even so the subdivision, particularly in Sections 3, 5 and 8, was considered inadequate.

Revised System

Vernon's four headings and NACE's eight headings have much in common and can be combined. If the NACE system were re-arranged and expanded to include the 1500 alphabetical subject headings that had appeared in the four

Abstract

A classification system intended as a basis for the compilation of a complete corrosion bibliography and for the recording and indexing of technical enquiries is described. It is based on the Abstract Filing Index, published by the National Association of Corrosion Engineers. Rearranged and expanded, it is capable of accommodating all the subject headings appearing in the corrosion bibliography, initiated by W. H. J. Vernon and subsequently maintained in card index form in the Chemical Research Laboratory, Teddington.

Classification and index are briefly described, and examples are given of their use and application. **1.4**

sections of the CRL Card-Index Bibliography during the period 1928-1950, the revised system would be capable of handling all corrosion topics appearing so far in the literature. This task was undertaken in the hope of producing a comprehensive classification capable of accommodating all known and future corrosion topics. The original 576 specific headings of the NACE system have been increased to over 800. This implies that at least half of the 1500 headings of the CRL Bibliography are too specific for the present system.

The general outline of the NACE classification has been preserved, in a slightly amended form, as follows:

1. General
2. Testing
3. General Principles and Characteristic Corrosion Phenomena
4. Corrosive Environments
5. Preventive Measures
6. Metal or Material of Construction
7. Equipment
8. Industries

Alterations will be found in Section 3 (General Principles and Characteristic Corrosion Phenomena), Section 5 (Preventive Measures) and Section 8 (Industries).

In Section 3 a sub-section on "Surface Phenomena" has been inserted, and the sub-section on "Electrochemical Effects" has been enlarged. In Section 5 the provision for paints has been increased from the original single heading "Primers" and a few headings under "Solid Organic Coatings: Uses" to a detailed classification containing 44 headings. The classification of inhibitors has also been much expanded; in addition, it has been considered expedient to place inhibitors for special solutions (antifreeze solutions, brines, sea-water, etc.) under a sub-division of the heading for these solutions in Section 4. "Suppression of bacterial action," although a "Preventive Measure," has been inserted under "Biological Effects" in Section 3 where it seems more appropriate. Also in Section 5, the general heading "Surface Treatment" has

been expanded to include "Cleaning for Special Purposes" and a more detailed treatment of surface conversion methods. Only minor alterations were made in Group 6, including the addition of a sub-divided heading "Metals and Alloys with Special Properties," and one for "Finely Divided Metals." The classification of plastics in this section was simplified, as it was considered unnecessarily detailed. Section 8, "Industries," has been expanded to include extra topics and subdivisions.

Numerical Index

The numerical index is comprised of a summary of the eight main headings, a summary of the 83 secondary headings and detailed schedules of over 800 specific headings.

Ranging from the general to the specific, main headings, sub-headings, and sub-divisions are indicated typographically by capitalization, type size, underlining and indentation. Headings are also differentiated numerically, with letters in the fourth and sixth positions for clarity. Figures and letters in the fifth and sixth positions are in parentheses. Further sub-division under any heading can be obtained by putting general topics first, followed by alphabetical specific topics.

Typographic head arrangements are illustrated in Figure 1. Thus an abstract on the theory of the oxidation of copper should be placed under 3.2.3 b (2) (b) copper.

Related headings, which might provide alternative positions for the placing of any topic, are indicated as far as possible in the numerical classification and in the alphabetical index. Additional general cross references can be inserted in the card index as it is compiled.

As far as possible the system has been constructed for future expansion by headings entitled "other." New headings may be inserted also.

Alphabetical Index

The alphabetical index to the classification contains all terms mentioned in the numerical index plus a few specific topics given as cross references. Details concerning the arrangement and alphabetization of the index are given in the introduction to the classification.

Subject Placement

Classification has two meanings: it may signify the arrangement of topics into a classified system, or it may signify the allocation of a subject into the most appropriate position in such a pre-arranged system.

Classification, in the second meaning, has been described as an art. To become proficient in this art, one needs a certain instinct supplemented by considerable experience. A thorough knowledge is required not only of the classification system itself but also of the material to be classified. The guiding principle should always be that material is placed where it is most likely to be looked for. This requires, incidentally, that the user also should know the classification system well or should seek guidance when using it.

Figure 1—Typographic head arrangements of the numerical index.

Figure 2—Special card for classification and filing of technical enquiries on corrosion topics.

Classification Hints

A few general hints can be given on subject classification:

1. Neither the numerical index nor the alphabetical index should be used alone when a subject is being placed. If the alphabetical index alone is consulted, the entry may not be allotted to the position giving the correct context. If the numerical index alone is consulted, an alternative and possibly better placement may be overlooked.

2. Entries should be placed normally under a heading as specific as possible, provided that this heading covers the whole subject matter. The whole classification number should be used. (Further details concerning this are to be found in the introduction to the classification system.)

3. Subjects covering two or more topics of the same class should be put under a more general heading covering the required topics if possible. For example, an article concerning corrosion in industrial, marine and rural atmospheres should be placed under "Atmospheric Corrosion, General," 4.2.1. (This point should be

remembered when searching for a classified abstract.) There are, however, places in the numerical index where this is not possible. For example, there is no suitable general heading for "Corrosion by Inorganic Chemicals and by Organic Chemicals"; an abstract covering both these topics should be entered under both headings.

4. Subjects having two or more aspects will need a main entry with added entries (not cross references) under the alternate headings. Specific cross references should be avoided as time-consuming and irritating to the user although general cross references, referring to alternate sections of the classification where additional material may be sought, may be inserted usefully into the card file. Many such general cross references are already provided in the numerical index.

Filing an Abstract

The following recommendations, though not strictly referring to the use of the classification system, may be helpful.

1. An abstract should be classified not only by its title, which may be misleading or inadequate, but also by its con-

tents. Significant words in the body of the abstract should be underlined to clarify the reason for the classification.

2. The abstract card is given the appropriate classification number and filed numerically. All cards of the same number should be filed chronologically by year of publication and alphabetically by author under each year.

3. Added entries, bearing the title, author and reference only, should preferably be on cards of a different color from those used for the main entry. The first card should bear the main classification number, followed by those of the added entries. Each subsidiary card should bear its own number first, followed by the main entry number second and underlined so that the main entry can readily be located and consulted for further details.

Preparation of Supplementary Indexes

As topics of a specific nature, not occurring in the index to the scheme, and those involving proper names (as of processes, alloys, etc.) are filed in their appropriate places, a supplementary index of these terms should be compiled so that the topic or term can be located readily and so that subsequent entries of the same term are put in the same place.

An author index should be compiled as the entries are made, the author's name being referred to the appropriate classification number and the year of publication of the articles: e.g., "Smith and Brown 6.3.3 1934" with a second card "Brown (with Smith) 6.3.3 1934."

The second card should not be labeled "Brown *see* Smith." This causes the user extra work and possible irritation.

Technical Enquiries Recorded

To maintain a classified record of technical enquiries on corrosion topics, a special card has been designed to facilitate the filing of such material. This is reproduced in Figure 2.

The eight blocks at the top of the card correspond to the eight main headings of the numerical index. Appropriate details are entered as fully as possible on the card which is then classified and filed in the usual way, added entries being made on colored cards. An index of the names of the individuals or organizations seeking advice should also be compiled.

The space at the bottom of the card labeled "Report" is for any information which may be received from the enquirers concerning the results of the initial advice. This is regarded as an important part of any advisory service. By systematically following up enquiries, a body of information can be built up concerning results obtained in the field.

This system of recording advisory services has several advantages:

1. A past enquiry can be found readily from a knowledge of either the enquirer's name or the subject of the enquiry.

2. Cards can be tagged to show which enquiries are still pending or which need follow-up action.

3. Advice once given but forgotten in detail can be recovered readily.

4. Advice that has proved unsound can be amended for future use.

5. Topics frequently recurring can be noted, and possibly some research can be undertaken on them.

Conclusions

This classification is presented as a workable system that should accommodate all current and future corrosion topics. It has been used in the Chemical Research Laboratory to classify about a thousand enquiries and several thousand abstracts.

The writer is aware that the system still contains imperfections and inconsistencies in spite of many emendations. Perfect abstract classification is, of course, an impossibility, but the present system might have been improved had it been possible to devote more time to expanding it. It is hoped that any remaining inconsistencies will not be considered unreasonable and that the system will prove to be of use to other workers in the field of corrosion.

Acknowledgments

The writer wishes to thank W. H. J. Vernon for his interest in the system and the Publication Committee and the Abstracts Sub-Committee of the National Association of Corrosion Engineers for permission to make use of their Filing Index.

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DISCUSSIONS ON TECHNICAL ARTICLES ARE SOLICITED

Discussions on technical articles published in Corrosion will be accepted for review without invitation. Discussions must be constructive, accompanied by full substantiation of fact in the form of tables, graphs or other representative data and be submitted in three typewritten copies. In cases where illustrations are submitted, at least one copy of figures should be of a quality suitable for reproduction.

Authors will be sent on request a copy of the NACE Outline for the Preparation and Presentation of Papers.

Discussions will be reviewed by the editor of Corrosion and will be sent to the author of the paper discussed for his replies, if any. Publication will be in the Technical Section with full credit to the authors together with replies. Discussions to papers presented at meetings of the association may be submitted in writing at the time of presentation or later by mail to the editorial offices of Corrosion, 1061 M & M Bldg., Houston 2, Texas.

Laboratory Methods for Determining
Corrosion Rates Under Heat Flux Conditions*

By A. O. FISHER and F. L. WHITNEY, Jr.

Course Pursued In Study

DURING DEVELOPMENT of Monsanto's corrosion program, a scarcity was observed of heat flux-corrosion data which engineering personnel responsible for materials selection could reliably use. Because data are not available, unsatisfactory and uneconomical materials have been used. Of specific interest was the effect of temperature as related to expanding production per capital dollar which applied not only to new processes or process change but to existing equipment.

Primary objective of this investigation was to relate the corrosion rate of a metal surface which is transferring heat to either the amount of heat flowing, the skin temperature or both and to develop a satisfactory laboratory test method for this purpose. A secondary objective was to demonstrate the inadequacies of the conventional immersion tests for predicting corrosion rates for heat transferring surfaces.

Background Theory

A literature survey on this subject revealed that very little information has been reported on corrosion rates under heat flux conditions and methods for their determination.

After some thought on the matter, it was postulated that perhaps heat flux is not the variable to be studied but rather the temperature of the metal surface. If this could be proved experimentally, the problem would resolve to determining the skin temperature effect on corrosion. All subsequent testing procedures then could be modified as a conventional immersion test held at the appropriate temperature. Then temperature corrosion curves could be developed easily for various metals in specific environments.

Obviously, proving this postulation necessitates considerable research, and at present this goal has not been achieved. After this test program was begun, it was believed that some practical heat flux corrosion testing techniques had been developed which would be helpful in solving field problems involving heat transfer. That information is presented in this paper.

In planning a laboratory program of this nature, it is necessary to consider the application of the data obtained. For example, a design engineer is accustomed to thinking of heat flux (Btu/hr/sq ft) for the transfer of heat in designing a piece of equipment and is less apt to think of the operating temperature. On the other hand, production personnel

Fisher   **Whitney**

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F. L. WHITNEY, JR.—Mr. Whitney, 1955-56 president of NACE, has been active in sectional, regional and national affairs of the association for many years. He is manager of the Corrosion Section, Engineering Department, Research and Engineering Division, Monsanto Chemical Co., St. Louis. His activities include not only corrosion engineering but he has been active in developing and participating in corrosion education activities. He obtained a BS in chemistry from Norwich University in 1930. Prior to his employment with Monsanto he was with E. I. duPont de Nemours & Co., Inc. in various capacities.

are more apt to think of operating temperatures and often are not aware of the actual heat transfer rates. Thus a satisfactory laboratory program for a study of the heat transfer effect on corrosion should provide a means of determining skin temperatures and heat flux rates. In this way laboratory data can be helpful to the design engineer and the production superintendent. This paper describes some of the testing techniques which have been investigated for these purposes.

In all tests, specific heat of the metal and its coefficient of heat transfer are assumed to remain constant within the temperature ranges employed. In most cases actual heat flux calibrations were made at the operating temperatures, thus eliminating some of these variables.

Testing Techniques

Resistance Heating Heat Flux-Corrosion Tests

The first heat flux corrosion investigation concerned the rapid failure of a direct oil fired cast iron vessel eight feet in diameter and about nine feet high with a hemispherical bottom. A molten inorganic salt was prepared at 300 C (572 F) in this vessel. The finished product was removed by overflow. No external agitation was employed; all cir-

Abstract

Laboratory techniques for testing the effect of heat flux and skin temperatures upon corrosion rates of 316 stainless steel, steel and cast iron in various environments are described. Advantages and disadvantages with supporting evidence are given for three practical approaches to this fundamental study in the laboratory.

Based on the data obtained, skin temperature rather than heat flux has been found to be the controlling factor in the corrosive environments investigated. Heat removed from the corroding surface through agitation and/or other methods appears to be the most practical means of increasing heat flux input without excessively increasing corrosion rate.

Preliminary results indicate the superiority of these techniques over the customary immersion tests for obtaining corrosion data involving heat transfer conditions. Continued research on these methods should eventually lead to the development of limiting skin temperatures for various metals in specific environments. Practical application of the data should form a sound basis for predicting plant corrosion rates in heat transfer equipment.   2.3.7

culation resulted from natural convection currents. Under normal production rates, pot life was six to eight months. When production was increased 150 percent, pot life was reduced to less than three months. Failure was by excessive pitting of the 4-inch thick hemispherical bottom. Since replacement pots were costing $6000 installed, the immediate concern was to determine what maximum production rate would maintain the previous six to eight-month pot life.

An engineering study of the field unit showed that, although fire box temperatures had been taken, frequent burn-out of the thermocouple left control largely to guess work and the measurement of oil consumption to the burner. Production records revealed that at the higher production rate heat flux through the pot was about 15,000 Btu/hr/sq ft. Data for the lower production rates were not available.

Since neither inside nor outside skin temperature was measured, primary concern in setting up the laboratory heat flux corrosion apparatus was directed toward heat flux rates. It was concluded that the best way to determine the effect of heat flux on corrosion in the laboratory would be to use a high amperage, low voltage a-c current such that the test specimen would generate heat by its resistance to the electrical current flow. This would afford a high heat transfer rate which easily could be calculated from the electrical power input to the specimen.

The laboratory set-up was designed as follows: a 3½-inch long, ⅛-inch diameter machined cast iron test spindle was clamped between two over-sized electrodes connected to the terminals of a ½-killowatt transformer. The 110-volt power input to the transformer was controlled by a Variac. The electrodes and test spindle were immersed in the molten
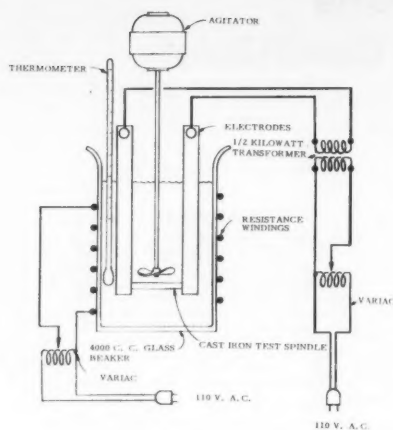
Figure 1—Schematic diagram of electric resistance heating for heat flux-corrosion testing.

Figure 2—Corrosion of cast iron in molten salt vs heat flux rate with electrical resistance heating.

Figure 3—Cross sectional schematic diagram of tubular heat flux corrosion testing unit.

salt, the temperature of which was maintained by a separate resistance wiring circuit wound on the outside of the container. This equipment is shown in Figure 1. Mild agitation was provided to prevent stratification of test solution and to simulate plant conditions. Voltage and amperage readings were made at the electrodes and corrected for current leakage through the molten salt before any heat flux calculations were made. Control specimens having no heat flux were included in each run. Data obtained with this method are shown in Figure 2.

From the isotherms in Figure 2 it was concluded that heat flux is critical at about 9,000 to 12,000 Btu/hr/sq ft when the salt temperature is kept at 300 C (572 F). If the salt temperature is lowered to 265 C (329 F), corrosion is reduced to one inch per year or less at this heat flux rate, a low rate considering the field failures calculated at 8 to 12 inches per year. Because a variation in salt temperature influences corrosion rate at the same heat flux rate, it can be inferred that test specimen skin temperature controls rate of corrosion. Because skin temperature was not measured in this particular method, this conclusion has to be drawn indirectly. The inflection point on the 300 C isotherm at 10,000 Btu/hr/sq ft is probably the beginning of salt dehydration. Certain data have indicated that dehydration is effected at 340 C. The difference in corrosion between a heat flux specimen and a conventional immersion specimen in the same salt solution illustrates the need for a heat flux test to duplicate actual skin temperature conditions.

This testing technique proved satisfactory from a production standpoint because necessary corrections could be made in the field by adjusting oil input (heat flux) to the pot. From an academic standpoint, however, the method was incomplete because no skin temperatures were taken. The disadvantages included (1) in other more conductive environments electrical leakage might produce undesirable effects, (2) heat distribution on the test rod was not uniform,
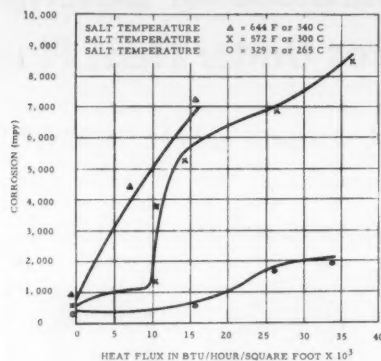
being higher at the center and (3) voltage corrections were high (30 percent) compared with current corrections (3 percent). This made heat flux calculations less accurate than desired. Another factor not considered was the effect of electron excitation of the metal caused by electrical current passage. It is not known whether this influences the corrosion rate.

Tubular Heat Flux Corrosion Tests

The laboratory apparatus consisted of a quartz heater placed in a tubular test specimen immersed in the test solution as shown in Figure 3. The two liter flask is fitted with agitator, condenser and a hook on the thermometer well to hold the control (non-heat transferring) specimen. Heat flux rates through the tube were adjusted by a Variac connected to the quartz heater. With this method, heat flux rates through the tube must be determined experimentally for various Variac settings. The pencil-type quartz heater used in the experimental work delivered 300 watts with a 110-volt input.

Data obtained with this testing technique are shown in Table 1. From these data it appears that the corrosion of 316 stainless steel is sensitive to heat flux conditions in 77 percent H_2PO_4. This phenomena was investigated more thoroughly with the modified disc testing technique, the results of which are given later.

The advantages of this particular test unit can be summarized briefly as follows:

1. A controllable heat flux source causing no objectionable complications resulting from electron excitation which might influence corrosion.

2. A suitable method for the simultaneous testing of vapor, liquor and interface areas of a specimen.

3. A reproducible method for testing tubular stock.

The greatest objection to this testing method is that no temperatures are taken. This is possible but rather complicated for several reasons. For example, radiation from the quartz heater would invalidate temperatures taken inside the tubes unless special shielding
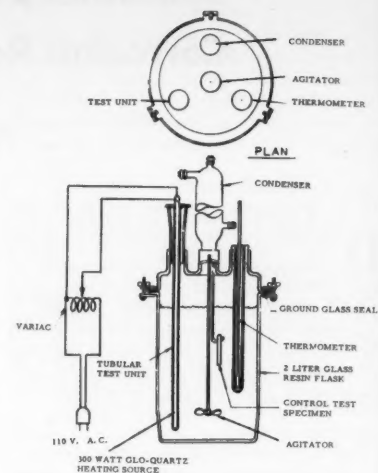
was provided and the thermocouple was properly attached to the inside of the tube specimen.

Excessive weight of the test specimen (150 gm) is another disadvantage since it affects the accuracy obtainable on an analytical balance.

Modified Disc-Heat Flux Technique

After consultation with design engineers, it was concluded that a more satisfactory laboratory heat flux corrosion apparatus would have to provide a method for measuring or calculating skin temperature of the corroding metal. This led to the search for a third type of apparatus.

The AEC at Hanford, Washington, had constructed and successfully used a boiling heat flux corrosion testing apparatus.[1] Many of the features of this AEC apparatus were incorporated in the design of the third type of heat flux testing apparatus which has been named the modified disc-heat flux technique.

This apparatus consisted of a one-liter flask with a 1-inch glass pipe bottom outlet. The flask also was fitted with a thermocouple well, agitator blade and a condenser. A 1¼-inch by 1¾-inch by 1¼-inch test plate was fastened to the glass pipe with a standard glass pipe flange. Heat was supplied by a soldering iron; the tip was replaced with a flat machined aluminum head clamped to the underside of the specimen by the other half of the pipe flange as shown in Figure 4. A schematic diagram showing this equipment and related cooling and auxiliary heating devices is given in Figure 5.

Two thermocouple holes were drilled in the aluminum head for heat flow measurements. A thermocouple hole also was drilled into the test plate edge extending to its center for specimen temperature readings. Skin temperature can be calculated when the heat transfer through the metal, the metal thickness and the thermal conductivity of the metal are known. The standard Fourier equa-
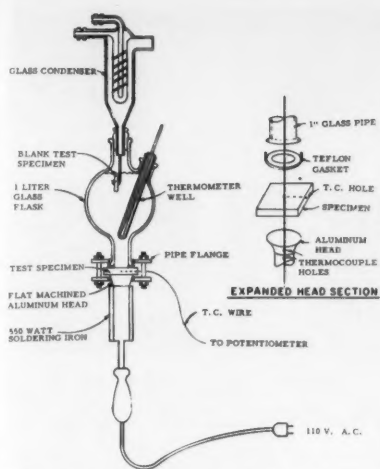
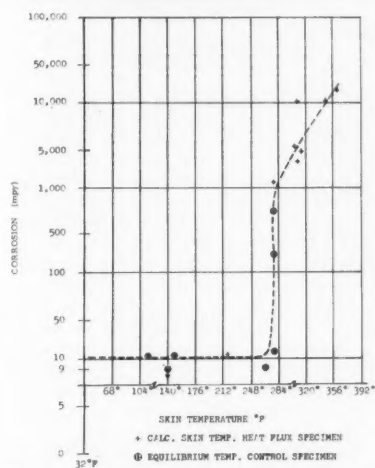Figure 4—Schematic diagram of boiling disc type of corrosion apparatus.

Figure 6—Corrosion of 316 stainless steel in fertilizer grade 77 percent H_3PO_4 at various skin temperatures. The modified disc technique was used.
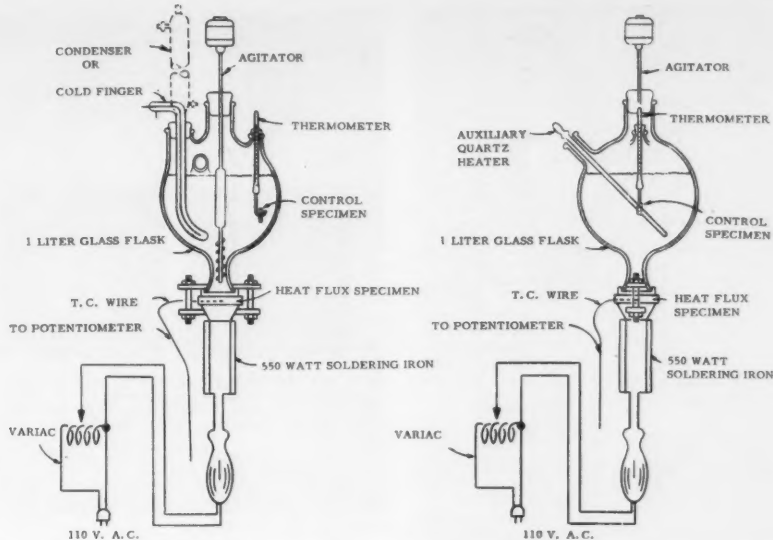

Figure 5—Schematic diagrams of modified disc heat flux corrosion apparatus for temperatures below boiling and at boiling point. The heating iron is mounted vertically. The left diagram shows a sectional elevation; the right diagram a view rotated 90 degrees.

TABLE 1—Corrosion of 316 Stainless Steel in Fertilizer Grade 77% H_3PO_4 Under Varying Heat Flux Conditions*

Run No.	Hours Duration of Test	Heat Flux Rate Btu/hr/ft²	Acid °C	Temp °F	Corrosion MPY	
					Heated Tube	Control Tube (No Heat Flux)
1	24	2,500	110	230	16	12
2	24	2,700	118	244	160	19
3	24	2,800	120	248	366	17
4	24	3,800	137**	279	856	399
5	6.5	16,700	137**	279	1860	940

* Data from tubular heat flux test unit.
** Boiling point of the acid.

tion for heat conductivity calculation was used for this purpose. Heat flux through the metal disc was determined experimentally for the unit by running heating and cooling curves over a range of Variac settings which control the soldering iron current. Temperature readings in the aluminum head can also be used to measure heat flow through the specimen but require correction for radiation losses at the specimen holder (pipe flange).

Agitation across the face of the heat flux specimen measured empirically was approximately 0.6 fps expressed as water at room temperature. The flow at the control specimen was about 0.1 fps. At these low flow rates, the effect of agitation was considered insignificant. At high skin temperatures and high heat flux, corrosion flow patterns were observed on some specimens in certain environments. In the higher temperature ranges the effect may be due primarily to nucleation of vapor bubbles at the metal surface. The effect of velocity is an important consideration; laboratory studies are in progress at these low agitation rates to determine the effect on

corrosion data obtained with this technique.

Field problems discussed below demonstrate the practical value of this method.

A 316 stainless steel coil handling 110-pound steam was to be used for heating a liquid aromatic material. Liquid temperature was to be held at 135 C. The coil was designed to transfer 5,000 Btu/hr/sq ft. The question to be answered concerned the suitability of 316 for this service.

In solving this problem, soldering iron current was adjusted to give a calculated metal skin temperature of 165 C which is approximately equivalent to that of 110-pound steam. At this temperature the 316 stainless steel test specimen transfers 30,000 Btu/hr/sq ft in the laboratory apparatus. Contents of the test flask were kept at 135 C by means of auxiliary heat from a quartz heater similar to the one previously described. A control specimen of 316 stainless steel was suspended in the 135 C liquor for comparative purposes. This specimen passed no heat but maintained an equilibrium skin temperation with the environment. This was the conventional immersion test.

After 24 hours of exposure, the 316 stainless steel heat flux specimen corroded at 12 mpy compared to less than 1 mpy for the control specimen. This was

an excellent comparison between a heat flux test and a conventional immersion test. The difference between a corrosion rate of 12 and 1 mpy can be an important factor in the economy and design considerations of an expensive or low heat transferring alloy. In this instance 316 with 12 mpy was considered justifiable for the service intended.

The modified disc test unit was used also to study the corrosion of 316 stainless steel in 77 percent fertilizer grade phosphoric acid. Results of this investigation are shown in Figures 6 and 7. In Figure 6 corrosion rate is plotted vs temperature; in Figure 7, corrosion rate vs heat flux. In Figure 6, a sharp rise in corrosion rate is shown coincidental with the boiling point of the H_3PO_4. This increase in corrosion was believed to be caused by a nucleation of vapor bubbles occurring on the specimen surface. The vapor interface provided a higher skin temperature because there was a reduction in area of the liquid film for conducting heat away from the specimen. Under these conditions and within certain limits, heat flux effect and skin temperature might be considered synonymous.

In Figure 7 it should be noted that corrosion was mitigated somewhat when a cold finger was inserted in the flask to lower acid temperatures. Although the
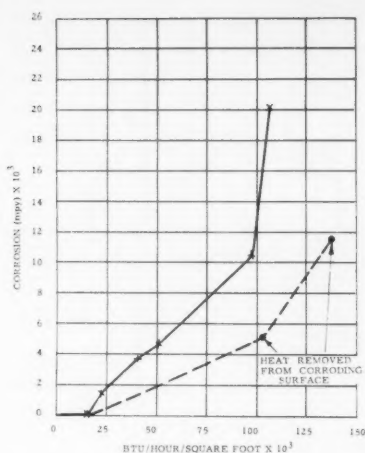
Figure 7—Corrosion of 316 stainless steel in fertilizer grade 77 percent H_3PO_4 at various heat flux rates. Modified disc technique was used.

Figure 8—Data on 76.3 percent H_2SO_4 six hour tests. Top row: Specimen A. 79 C solution temperature, 15 mpy; Specimen B, 91 C, 710 mpy; Specimen C, 126, 932 mpy; Specimen D, 158 C, 862 mpy. Bottom row: Specimen A, 103 C, 2140 mpy, 20,000 Btu/hr/sq ft; Specimen B, 126 C, 4380 mpy, 25,000 Btu/hr/sq ft; Specimen C, 181 C, 27,500 mpy, 42,000 Btu/hr/sq ft; Specimen D, 185 C 94,800 mpy, 63,000 Btu/hr/sq ft.

temperature readings of the heat flux test specimen in these two cooling tests did not show any reduction, the 60 C liquor in contact with the heat flux specimen presumably lowered the skin temperature and as a result lessened corrosion.

In another field problem, the effect of metal temperature upon the corrosion rate of steel in impure 76 percent H_2SO_4 was to be determined. Some corrosion rates and photographs of four specimens in this study are given in Figure 8.

Results of a study of 304 stainless steel in 65 percent HNO_3 are shown in Figure 9. The heat transferring surfaces corroded faster than the controls at the same temperature. Reasons for this difference are unknown at present, but velocity differences are suspected.

To determine the effect of velocity, the corrosion rates of heat flux specimens were measured while *no* heat was flowing. Heat was supplied to the solution by a submerged quartz heater. At 120 C solution temperature, boiling point for 65 percent HNO_3, the non-heat transferring heat flux specimen corroded at an average rate of 11 mpy. This compared with about 14 mpy for the specimen transferring heat at 120 C and 9.0 mpy for the control at 120 F. These data indicated that agitation alone did not account for the entire difference in corrosion rate between heat flux and the control specimen in this media. A more thorough investigation is necessary to prove whether this phenomena is characteristic of all heat transferring surfaces.

These results were sufficiently encouraging to set up a battery of four identical units in the laboratory for expediting test data development. This equipment is pictured in Figure 10. The electrical meters shown measured voltage and current to the individual soldering irons to facilitate duplicate settings from run to run. Either condensing or cooling units can be used in this equipment, depending upon the desired temperatures and heat flux conditions to be maintained.
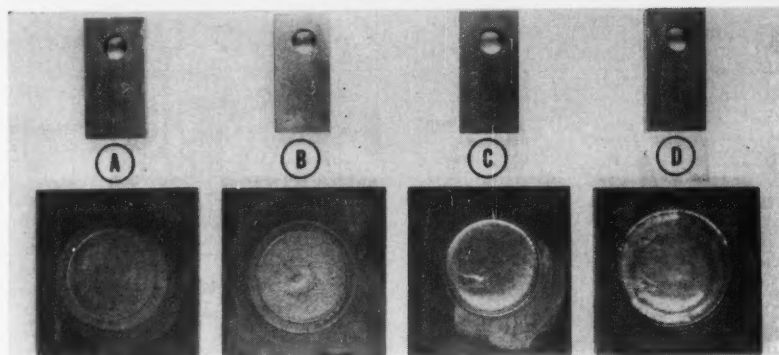
This work showed that close contact

between disc and aluminum heating head was needed to obtain good reproducible results. Both surfaces had to be thoroughly clean and polished to a 120 grit finish. To assure uniform close surface contact and to prevent glass nozzle breakage, an automatic torque wrench was used to tighten the heating head. The wrench was set at 25 pounds, the maximum pressure to insure best results.

With the modified disc-heat flux testing technique, heat flux rates over 100,-000 Btu/hr/sq ft and metal temperature to 260 C have been attained. Under these conditions calculated skin temperatures may be as high as 180 C, depending upon the metal. With heating heads of different metals and higher temperature gasketing materials, temperatures to 400 C can be obtained. Accuracy of the heat flux data with the techniques presently employed is probably within 10 percent of the heat flux rates given in this paper. For example, at 25,000 Btu/sq ft, readings may be off ± 2500 Btu/hr/sq ft. At 50,000 Btu/hr/sq ft, this difference is 3500. Cost of one test unit including all auxiliary equipment is about $100.

Advantages of Modified Disc-Heat Flux Technique

1. Speed: Because small test samples were used, accurate weight loss determinations were made quickly. Representative data have been obtained within eight hours. Normally 10-day test periods are considered a minimum to develop types of attack and representative rates. In the case of heat flux specimens, 24 hours may be sufficient.

2. Accuracy: Because analytical conditions prevailed in this test, accuracy was commensurate with the equipment employed. Because the surfaces on the heat side were unaffected, the corrosion rate was measured on those associated only with the process side or chemical environment. When heating media such as electric resistance (thru the specimen), steam, oil or hot gases were used, the heating side always was affected by corrosion or contamination resulting in less accurate weight loss measurements.

3. Reproducibility: Because the test equipment was assembled always in the same fashion and under controlled con-
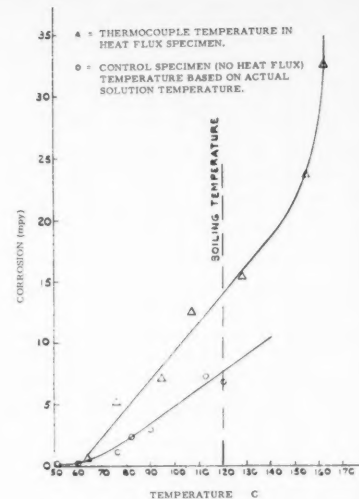

Figure 9—Corrosion of 304 stainless steel in 65 percent HNO_3.

ditions, good reproducibility was obtained when measured under equivalent conditions.

4. Simplicity: The test units were made of standard laboratory equipment simple to make and inexpensive to assemble. Operation was uncomplicated, and standard analytical procedures were employed.

5. Simulating Plant Conditions: As far as heat transfer was concerned, the method reproduced accurately the heat flow through metal walls and its effect on corrosion. The method was more effective in solving plant problems in the laboratory than the conventional immersion methods.

6. Pressure Systems: Because such high skin temperatures can be used in this method, elevated temperature tests can be conducted at or below boiling without resorting to high pressures to attain these temperatures. This not only simplifies the testing technique but also reduces cost and permits more extensive testing with greater accuracy of results.

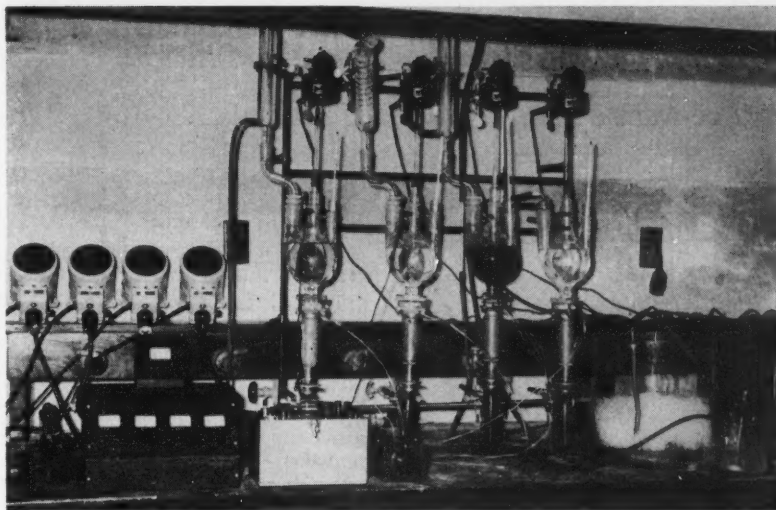Limitations of this technique are given below.

Figure 10—Modified disc-heat flux equipment.

1. Temperature Measurement: Actual skin temperature was not measured because of operational difficulties and had to be calculated. The technique does not provide a truly accurate method of calculating the skin temperature of the metal adjacent to the environment. The accuracy in this respect is limited to the thermal conductivity of the metal, the temperature drop through the metal wall and the calibration techniques used for the heat flux determinations. Practically, however, the accuracy probably was within 10 C and hence suitable for field evaluations. Where critical temperature conditions may be sharply defined as with H_3PO_4 and shown in Figure 6, greater accuracy may be required to avoid costly damage to equipment.

2. Velocity: The technique was not intended to study the effect of velocity. Agitation was designed primarily to provide movement over the surface to aid heat transfer and to prevent deposition of solids on the heat transfer surface. This was accomplished and the rate was 0.6 fps, well below the turbulent region. The fact that some flow patterns were observed on specimens at certian high temperatures probably was an effect of convection currents or a vapor nucleation rather than a stirring velocity. When the temperature is high enough to produce vapor at the metal surface, a sharp rise in temperature at the immediate metal surface will result because of the poorer heat transfer.

This phenomena is being studied in relation to the practical aspects of this technique.

Conclusions

Of the three testing techniques described, the modified disc method is considered the most practical for obtaining laboratory corrosion data under heat-flux conditions. This method affords an inexpensive laboratory tool for predicting the effect of heat flux and/or skin temperature upon corrosion.

A number of exploratory tests on H_2SO_4, HNO_3, acetic acid and H_3PO_4 using the modified disc-heat flux testing technique generally have confirmed that skin temperature of the metal is the major controlling factor in corrosion—not the amount of heat flowing through the metal. This appears to be the case at least in lower temperature ranges.

Acknowledgment

The authors acknowledge the excellent assistance and suggestions made by F. E. Cole in carrying out the laboratory work covered by this paper.

Reference

1. Private communication, Norman D. Groves* to A. O. Fisher, May 3, 1955.

Addendum

Questions on performance of the 1-inch disc prompted additional development with a 2-inch diameter disc. The new 2-inch unit is similar to the 1-inch unit except that a 2-inch diameter glass pipe fitting has been substituted for the 1-inch fitting. This allows a larger area of specimen (four times) to be exposed to the corrodent. The only other change is a reduction in stirrer speed from 1750 to 350 rpm. A 2-inch unit is shown in Figure 11.

With the 2-inch unit, operation is possible at lower heat flux ranges (5000 to 30,000 Btu/hr/sq ft) with the same accuracy as was possible with the 1-inch unit when 20,000 to 120,000 Btu/hr/sq ft were flowing at the same heat input setting. This is a distinct advantage in most test applications because plant equipment is usually operated in these lower ranges. The larger test unit necessitated the purchase of a 2-kilogram balance so that specimens over 200 grams could be weighed with a sensitivity of ±0.0004 grams.
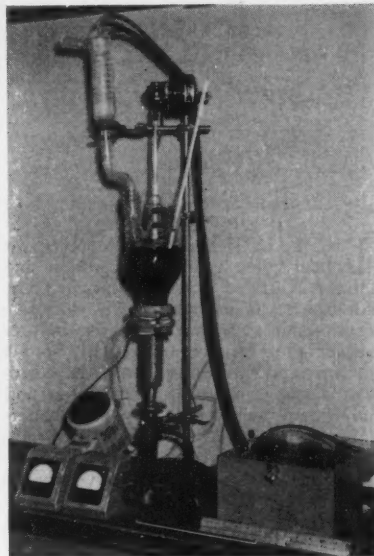
Figure 11—Two-inch unit for heat flux ranges from 5000 to 30,000 Btu/sq. ft.

Reduction in stirring velocity to 350 rpm was considered necessary because of flow patterns observed on specimens in certain environments in the 1-inch diameter unit. This was particularly true in sulfuric acid of various strengths (see Figure 8). Flow patterns were not observed on stainless steel coupons exposed in 75 percent H_3PO_4 and 65 percent HNO_3, indicating that perhaps velocity is not a major factor of corrosion in these environments under the test conditions. A reduction in stirrer speed to 350 rpm produced approximately a 0.1 fps velocity (a reduction of five times) across the face of the heat flux corrosion specimen. This amount of agitation is sufficient to disburse the heat from the sample face without causing excessive erosion in the more agitation sensitive environments.

Laboratory calibrations of the 2-inch unit on glycerine indicate that accuracy of heat flux measurements is about ±5 percent. During the calibration work on copper specimens, this metal was quite susceptible to rapid oxidation in air. For this reason, copper heating heads are not recommended over aluminum despite their greater heat conductivity. The work indicated that even with solution temperatures as low as 170 C in the flask, parts of the copper specimen exposed to the atmosphere oxidized at a rate of over 100 mpy. This amount of weight change on the atmosphere exposed parts of the copper specimen is enough to obscure any weight loss that would be caused by test solution in the flask.

At the present stage of development, a 2-inch diameter modified disc unit with slow speed agitation (0.1 fps) appears to be more adaptable to solving field problems in the chemical industry than the 1-inch diameter unit with high speed agitation (0.6 fps). The 1-inch unit perhaps is more suited to conditions where higher heat fluxes and high velocities are involved.

Influence of Temperature on Corrosion Fatigue*

By I. CORNET and SIMCHA GOLAN

Introduction

THE FAILURE of metal components under joint action of corrosion and fatigue is called corrosion fatigue. The atmosphere is an appreciably corrosive environment, and many service failures attributed to fatigue may actually be due to corrosion fatigue.[1] Because the corrosion fatigue problem is so wide spread and important, an investigation was undertaken to determine the influence of temperature on corrosion fatigue, particularly with reference to the corrosion fatigue mechanism.

To isolate the effects of temperature, those factors which affect corrosion fatigue must be recognized. These factors may be grouped as follows:[2]

1. Physical properties with special emphasis on notch sensitivity

2. Chemical composition and heat treatment

3. Time and rate of the stress applied

4. Nature and degree of stress applied

5. Nature of the corrosive medium

6. Presence or activity of dissolved gases such as O_2, H_2S, CO_2

7. Temperature

Extensive work by McAdam and others[3,4,5,6] has resulted in knowledge of the influence of the first four and has been summarized by Gough.[7] Nature of the corrosive medium and effects of dissolved gases have been studied by Speller[8,9,10] and by Wescott.[11,12,13]

The effect of temperature, although extensively investigated in regard to stress-less corrosion,[14] has been relatively neglected in studies of corrosion fatigue. Statements may be found in the literature[15] predicting corrosion behavior under cyclic stress conditions at higher temperatures on the basis of information available from stress-less conditions.

Gould[16] reported a definite temperature effect on steel wire corrosion fatigue in synthetic sea-water. As seen in Figure 1, reprinted from Gould's paper, endurance values of about 10 million cycles were approximately halved by raising the temperature from 15 C to 45 C.

As part of a study of corrosion fatigue inhibition in NaCl solution by zinc-yellow, Paul[17,18] reported temperature effects shown in Figure 2. The life of steel wire specimens at low and medium stresses in uninhibited solution (0.1M) was increased at 35 C and decreased at 50 C to slightly below the value for 23 C. At high stress there was no change at 35 C but an 11 percent increase at
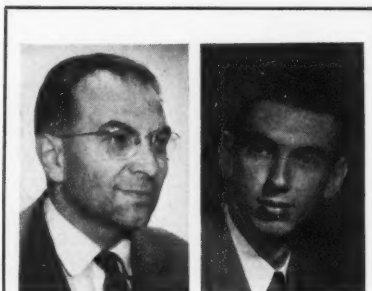
ISRAEL CORNET—Professor of Mechanical Engineering at the University of California at Berkeley. He has been a member of the NACE Awards committee and is active in the educational work of Western Region NACE, helping organize and conduct short courses and conferences on corrosion in California. He teaches corrosion at the university, is active in research, particularly on corrosion fatigue and stress corrosion.

SIMCHA GOLAN—Presently with Kaiser Engineers, Oakland, Cal. He received a BS in mechanical engineering from the University of California at Berkeley in June 1953 and did graduate work on the same campus receiving an MS in 1955. His master's thesis was titled "The Influence of Temperature on Corrosion Fatigue."

50 C. Paul explained these results on the basis of balancing increased penetration power of the chloride ion with a decrease in concentration of dissolved oxygen depolarizer.

Although Gould and Paul worked within the same temperature range, their results differ primarily because of differing test conditions. Gould applied the corrosive by a drip device to a small part of a wire; Paul had his specimen submerged. Also, Gould controlled temperatures by varying the room atmosphere; Paul controlled temperature in the solution by a heater and thermostat arrangement.

Further work on temperature effect on corrosion fatigue was undertaken to explain the discrepancies observed in Gould's and Paul's experiments.

Apparatus

The Kenyon rotating wire arc fatigue machine[19] was chosen as the most suitable because of its operation simplicity and easy adaptability for immersed corrosion fatigue tests.

The Kenyon machine, first developed in 1935, was originally intended for testing endurance strength of wires and properties of plated wires under corrosion fatigue conditions.[20] In 1942, Paul[17] adapted this machine for plain corrosion

Abstract

Effect of temperature on corrosion fatigue of two types of steel between 80 F and 180 F is discussed. All tests were single stage type in 2.5 percent NaCl solution. Apparatus used is described. Corrosion fatigue properties at 180 F were observed to improve over those at room temperature.

Apparatus discussed was versatile enough for fatigue tests under various conditions.

3.5.8

fatigue studies and found that the information obtained was interpreted easily.

In this machine, a wire is bent in a vertical plane by being passed through two bearings arranged symmetrically at an angle to the horizontal. One end of the wire is rotated by a motor, but the other end is free to rotate and slide freely in the bearing. Thus, flexural shear is eliminated, the distortion is pure bending and the curve assumed by the specimen is an arc of a circle. Stress on the extreme fiber is uniform throughout the sample and is inversely proportional to curvature radius. The failure occurs anywhere between the two bearings. The tendency of the wire to sag under its own weight was negligible. Acting as its own shaft, the wire does not undergo appreciable wear in the bearings.

This machine offers the following advantages, as noted by Kenyon:

1. Equipment and specimens are nominal in cost.

2. Operation is easy and simple.

3. There is no particular problem of failure at the gripping section or in bearings.

4. Vibrations are damped in the solution.

5. Fatigue breaks are not confined to one point.

6. The machine is self-calibrating due to the specimens assuming the form of a circular arc.

Stress on the extreme fiber of the specimen can be calculated using the equation[18]

$$S = \frac{Ed \sin \Theta}{C} \text{ lb/sq in.}$$

Where

E is the modulus of elasticity, psi

d is the diameter of the wire, inches

Θ is the angle the inclined bearing makes with the horizontal

C is the horizontal chord distance between the lower ends of the bearings, inches

A derivation of this equation is given in Appendix 1.

Preliminary work was done in an open tank of salt solution with partial immersion of the wire. Evaporation rate was excessive at higher temperatures, requir-

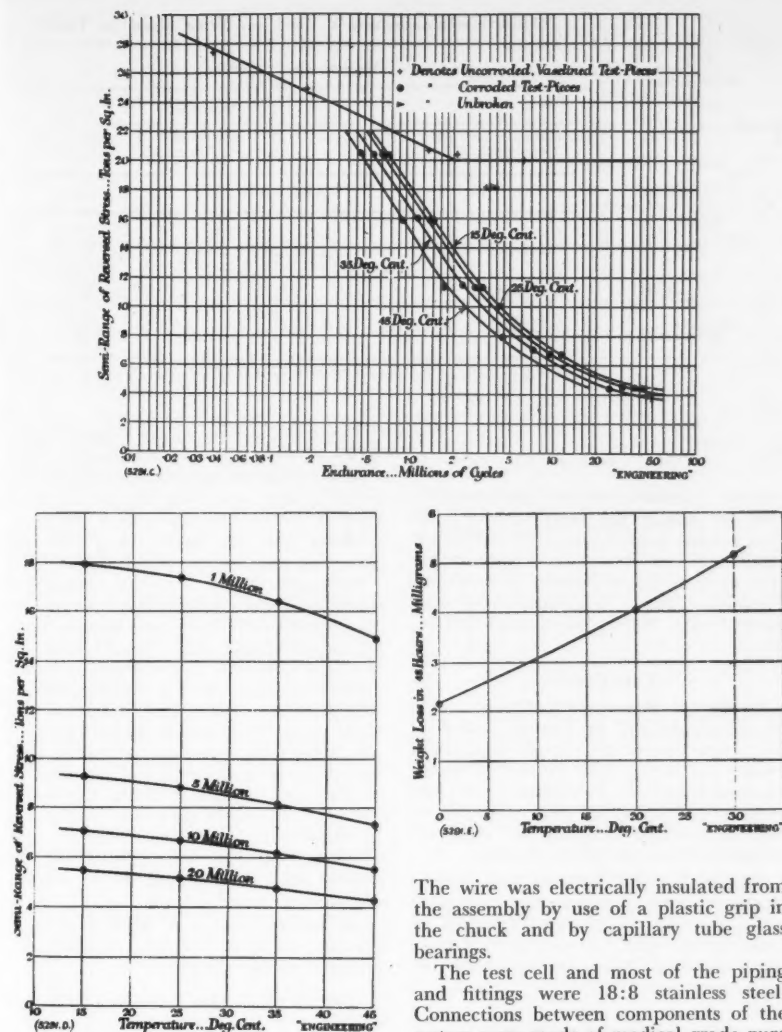Figure 2—Effect of temperature on corrosion fatigue.[17]

Figure 1—Influence of temperature on corrosion fatigue.[16]

ing frequent checks on the solution concentration and constant replenishing of distilled water. In the open tank there was a tendency for the wire to break at the solution surface where the wire was subject to differential concentration of oxygen and differential temperature effects. In the open tank at the surface, neither the oxygen gradient nor the temperature gradient could be controlled or readily determined. The system was re-designed to give reliable control of temperature and oxygen concentration.

The apparatus used is shown in Figure 3. The test cell rested on a scissor jack assembly to permit raising and lowering. Gaskets and seals maintained a few inches of water positive pressure of the atmosphere in the test cell. A bubbler arrangement fed nitrogen, oxygen or other gas into the test cell. Test cell temperatures were controlled to ± 2 F for any temperature in the range between room temperature and 200 F.

Solution level in the test cell was maintained by a baffle arrangement so that the wire test specimen was immersed.

The wire was electrically insulated from the assembly by use of a plastic grip in the chuck and by capillary tube glass bearings.

The test cell and most of the piping and fittings were 18:8 stainless steel. Connections between components of the system were made of medical grade pure latex tubing, ½-inch internal diameter and ⅛-inch wall thickness.

From the test cell the solution went to a sump where it was thermostatically controlled and heated. Solution was fed to a stainless steel centrifugal pump (1/15 horsepower) which circulated the solution at about 3 gallons per minute under operating conditions.

From the pump, solution was filtered to remove any suspended corrosion products. This filter was packed with glass wool wrapped in cheese-cloth. A valve and by-pass system made it possible to change filter packing while the equipment was in operation without interrupting circulation. Packing was replaced almost weekly when the equipment was in constant operation. From the filter, solution was pumped through a check valve into the test cell, completing the circuit.

The center of the rotating test wire passed through a pigtail trip rod attached to a micro-switch. When the test wire broke, one end deflected the pigtail trip rod attached to the micro-switch to stop the motor, counter, timer and pump. The test wire was rotated by a flexible shaft attached t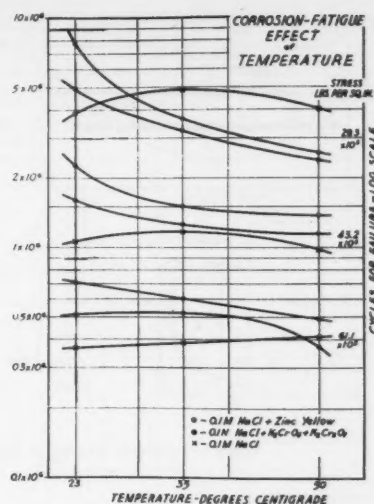o a gear reducer assembly driven by a ¼ horsepower d-c shunt motor. Direct current was supplied by a motor control, variable from 50 to 2400 rpm.

Equipment drawings and details are available.[21]

Test Procedure

Corrosive Agent

Corrosion fatigue tests were conducted with wires completely immersed in a solution 2.5 percent by weight (approximately 0.5M) sodium chloride in distilled water. This concentration was selected because of its high corrosivity and its small variation in corrosivity with change in concentration.[2]

During operation, concentration was determined by a hydrometer calibrated with a standard solution. Solution concentration was maintained within ± 0.2 percent tolerance. The pH was measured with a Beckman pH meter; all batches at all temperatures varied only between pH 6.5 and 7.5. The solution was changed at irregular intervals. Experimental data demonstrated that old solution used for five weeks did not change in corrosive activity. Paul observed this too, and stated that "apparently the chloride ion is so effective a penetrant of the surface film that changes in pH, within the above limits, are of no consequence."[17]

The filter kept the solution free of suspended matter so effectively that the solution remained clear, allowing excellent visibility through the test cell window.

Steel Wires

The two types of wire used, supplied by the Allegheny Ludlum Steel Corporation, Pittsburgh, Pennsylvania, are known commercially as Utica and Pompton steels. Both wires are classified as cold drawn drill-rod. As obtained, the wires had been polished to standard tolerances of ± 0.0003 inches and were in straight 3-foot sections, 0.039 inches in diameter. Manufacturer's data are shown in Table 1.
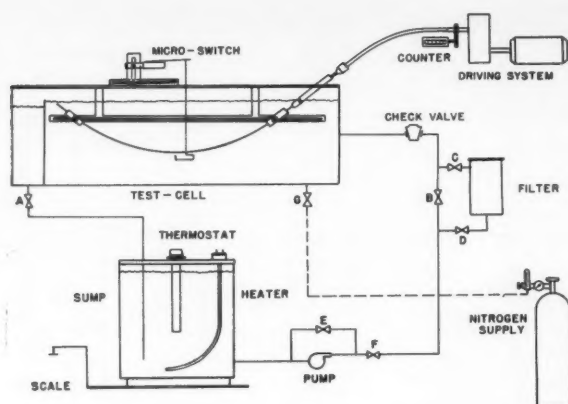
Figure 3—Schematic diagram of apparatus.

TABLE 1—Manufacturer's Data on Wire Used in Tests*

Mechanical Properties		
	Pompton	**Utica**
Ultimate Strength....................	105,000 psi	120,000 psi
Yield Strength......................	85,000 psi	105,000 psi
Analysis		
Carbon............................	1.2%	1.25%
Manganese.........................	0.25%	0.3%
Silicon............................	0.20%	0.3%
Tungsten..........................	......	1.4%
Chromium.........................	......	0.4%
Vanadium..........................	......	0.2%

* A modulus of elasticity of 30 x 10⁶ was assumed for both wires.

Test Procedure

The solution was brought to steady state at a selected temperature and oxygen concentration. Specimens, which arrived greased and wrapped, were cleaned with petroleum ether, further cleaned with isopropyl alcohol, rinsed with acetone and dried. Specimen wire was then bent into a 90-degree angle approximately 3/64 inches from one end to fit into the bakelite holder which fits into the chuck. At this point the cycle counter and clock were recorded, and circulation of solution was stopped by turning off the pump and shutting the discharge on the test cell. The test cell tank was lowered to its bottom position by use of a scissors jack, and the specimen was placed in position. When the wire and bakelite holder were inserted in the chuck, it was necessary to avoid contact between the wire and the stainless steel; such a galvanic cell would void the run. Also it was necessary to avoid kinking the wire while tilting the bearings to the required angle. When the specimen was in place, the tank was raised to its upper position and secured tightly. The pump was started again after the discharge valve on the cell was opened, and the motor was started. With the procedure used, a complete change of specimen could be made in about five minutes with no appreciable change in oxygen concentration.

A nitrogen bubbling system controlled the oxygen concentration, maintained in this study at about 0.7 ppm, corresponding to the concentration obtained when the system at 180 F was in equilibrium with the atmosphere. Trial-and-error adjustment of the nitrogen bubbling rate served to obtain this concentration at lower temperatures. Oxygen concentration measurements were taken at least once each day during operation by the Rideal-Stewart method,[22] which takes about forty minutes for each determination. A polarographic method probably would be preferable.[23]

This procedure was used for all the corrosion tests. Complete stress frequency curves were obtained at room temperature (80 F), 130 F and 180 F for both types of steel. Frequency used for corrosion fatigue tests was 360 cycles per minute. Corrosion-free tests were accelerated by raising the frequency to 1100 rpm because fatigue tests are not affected significantly by frequency change in the rpm range under discussion. To minimize corrosion, fatigue specimens were submerged in a trough filled with turbine oil.

Test Results

Results of this investigation are presented graphically in Figures 4 and 5. For more convenient comparisons, these results are shown with fatigue curves in Figures 6 and 7. In Figure 8, a cross plot derived from Figures 6 and 7 shows the temperature influence on specimen corrosion fatigue at various stresses.

Figures 9 and 10 present photomicrographs of typical longitudinal cross sections, showing distribution of attack at various temperatures. Photographs of specimens near the failure regions are shown in Figures 11, 12 and 13.

Discussion of Test Results

In Figures 4 and 5 curves are presented for the cycles to failure at various stresses for Utica and Pompton steel at three temperatures. Utica steel data shows a greater scatter than data for the Pompton steel, which may be due to the rougher surface of Utica steel.

Data for the Pompton steel shows no effects of raising the oxygen concentration from 1.0 to 4.5 ppm at 86 F or from 1.0 to 2.8 ppm at 130 F. In general, the oxygen concentration was held almost constant at all temperatures for the Utica steel to eliminate this variable. Paul[17] found steel wire corrosion fatigue life in sodium chloride solution about the same at 50 C as at 23 C (Figure 2); this he attributed to oxygen concentration decrease with temperature rise. Such an explanation would not apply to the present investigation in which oxygen concentration was relatively constant.

Figures 6 and 7 represent the average trends shown in Figures 4 and 5. Fatigue curves obtained in turbine oil are plotted for comparison. Trends are the same for Utica and Pompton steels. Curves at 180 F, for both steels, are to the right of the 80 F curves and level off earlier than the room temperature curves.

Figures 8, a cross plot of Figures 6 and 7, shows the temperature influence more clearly. As the stress becomes smaller, the ratio between specimen life before fracture at 180 F compared to room temperature becomes larger; at 45,000 psi this ratio exceeds two for both steels.

Corrosion fatigue is better understood when the main problem is recognized as one of corrosion. Protection against damage depends upon protective film formation and behavior. Internal and external conditions which set up electrochemical effects exert considerable influence on these films.[24, 25] Among important factors influencing corrosion fatigue are factors (1) which mainly affect the amount of dissolved oxygen reaching the metal surface, (2) which influence chiefly the localization of corrosion and the amount of pitting and (3) due to dissolved substances other than oxygen in the corroding solution.
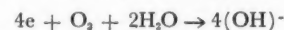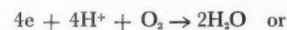
In normal corrosion when oxygen is present, corrosion reaction proceeds according to the equation

$$2\,Fe + O_2 + 2H_2O \rightarrow 2\,Fe\,(OH)_2$$

At the anodic regions the reaction is

$$2\,Fe \rightarrow 2\,Fe^{++} + 4e$$
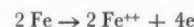
At the cathodic regions, the reaction is

$$4e + 4H^+ + O_2 \rightarrow 2H_2O \quad \text{or}$$

$$4e + O_2 + 2H_2O \rightarrow 4(OH)^-$$

The first of these cathodic reactions is favored in acid solutions where the electron jump tends to be to the hydrogen ion rather than to the oxygen. In neutral solutions, the electron goes to the oxygen which then reacts with the water dipole to give hydroxyl ions. In either case, oxygen is required for completion of the cathodic reaction.

Reaction rate depends on composition and relative motion of the solution, formation of films and temperature. These factors are interrelated and influence the corrosion rate by controlling the oxygen supply to the metal.

Temperature effect on the corrosion reaction does not ordinarily fit the usual rate equations. The influence of temperature is not always exponential as it would be for most chemical reactions, nor is it linear as it would be if influenced by certain physical changes alone. Some experimental corrosion rates increase with
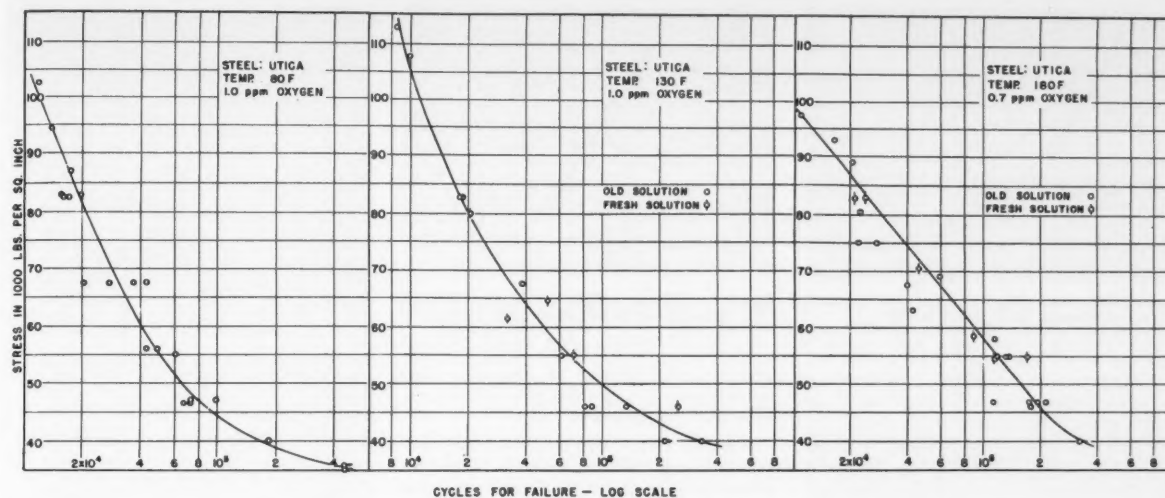
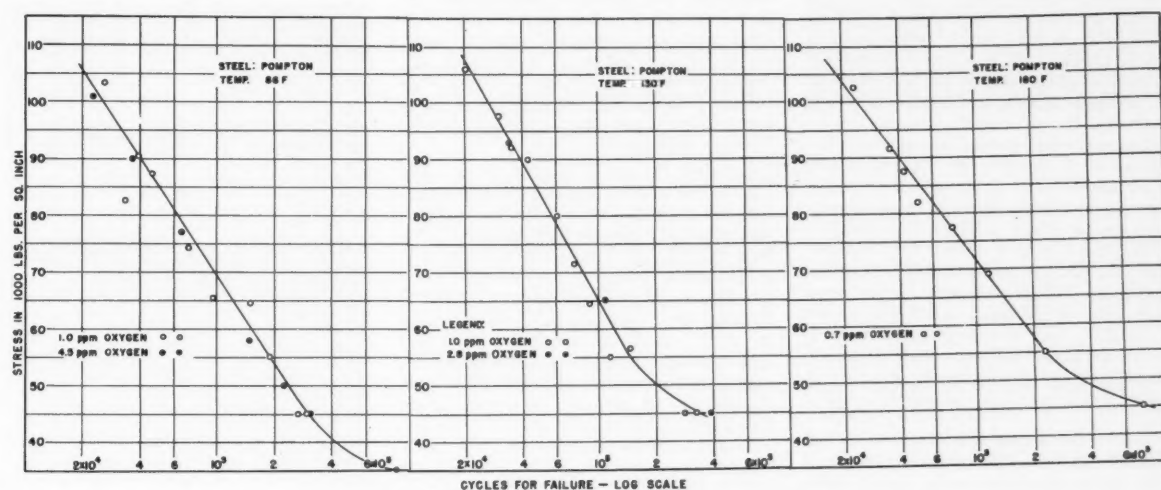Figure 4—Corrosion fatigue of Utica steel.

Figure 5—Corrosion fatigue of Pompton steel at 86 F, 130 F and 180 F.

temperature while others show a decrease. In some cases maxima are observed.[14, 17]

Corrosion consists of coupled chemical and physical changes, the rate of each step being dependent upon the supply of reactant from a preceding step. At least one step is electrochemical in nature. Each step in a coupled system exhibits a characteristic rate; the slowest of these determines the overall rate at any time. Each rate controlling step has some temperature coefficient which in turn will affect the corrosion rate.

The oxygen transfer mechanism from air to metal surface proceeds in three steps. First, the oxygen dissolves in the solution according to Henry's Law (the solubility decreasing while the rate of solution is increasing with temperature). Second, the oxygen is carried to the proximity of the metal by convection caused by agitation, and finally it diffuses to the metal surface through the quiescent film of liquid.

In most cases, the third step is the slowest one and thus controls the reaction rate. The diffusion rate of dissolved oxygen through the laminar boundary layer or film on the metal surface is directly proportional to film thickness. Temperature increase causes a decrease in viscosity which thins the film and speeds the amount of oxygen diffusing to the surface. Also, diffusion and solution rates of oxygen are shown[24] to be inversely proportional to viscosity to the 0.8 power. Also with increasing temperature, the oxide film becomes more porous, therefore speeding depolarization. In addition, the effect of salts upon the formation of surface films or coatings is more marked at higher temperatures. This may result in acceleration or retardation of corrosion rate, depending upon nature and distribution of the films. Pillon,[23] in a polarographic study of oxygen consumption of different metals, concluded that the values of activation energy obtained for reduction of oxygen

on lead, iron and zinc indicate that the reduction process overall rate is controlled mainly by oxygen diffusion toward the liquid-solid interface.

Many different theories for the mechanism of corrosion fatigue may be found in literature.[1, 2, 5, 26, 27, 28] Investigators agree that two main stages exist.

At the outset, corrosion produces a number of roughly hemispherical pits on the surface. If one of these happens to be more pointed at the bottom than its neighbors, the stress intensification will be greater at the bottom of this particular pit than at the bottom of the others. Since stress will make the iron anodic by distortion of lattice or by rupturing protective films, the electromotive force, working between the bottom of this pit and the aerated cathodic surface, will be greater than that operating at other pits. Thus, corrosion will be stimulated at the pit base, making it still more pointed and further raising the emf. Consequently, once started, this pit will fill with cor-
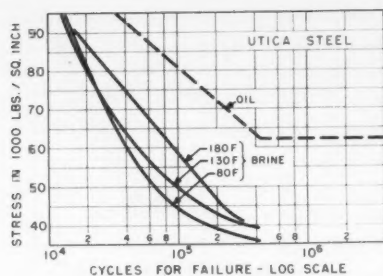
Figure 6—Corrosion fatigue of Utica steel in a brine solution at 180 F, 130 F and 80 F.
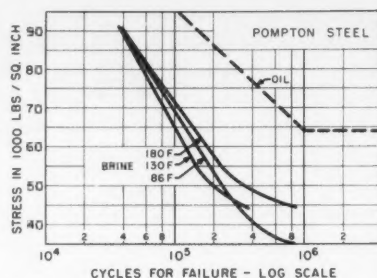
Figure 7—Corrosion fatigue of Pompton steel in brine solution at three different temperatures.

Figure 8—Effect of temperature on corrosion fatigue of Pompton and Utica steels.

rosion products to form a differential concentration cell in addition to the stress concentration developing at its base. The pit will propagate itself until the stress is above the endurance limit, thus reaching the second stage. From this point, simple fatigue will cause the specimen to fail.

There is at this point no well defined picture of corrosion fatigue based on solid state theory. Metal fatigue is considered to take place as follows: [29, 30, 31, 32]

Initially cyclic stress produces slip within grains. At early stages of fatigue these slip bands may be readily removed by electropolishing. As cyclic stressing continues, the slip bands become deeper and more pronounced. After some five percent of the fatigue life (in copper and in aluminum) the electropolishing which normally removes slip bands is no longer 100 percent effective. Some short lengths of slip bands persist unless surface layers up to 30 microns are removed by electropolishing. These persistent bands grow with further cycling, crossing grain boundaries and developing into microcracks at about half the normal fatigue life. The microcracks grow into cracks which propagate to produce ultimate failure.

Studies by Wadsworth, Thompson and Louat[30] and by Harries[31] have shown that cracks nucleate under cyclic stress and develop on the surface, presumably because flow occurs successively on slip planes that intersect each other near a free surface. Under stress influence dislocations move. Groups of dislocations pile up at barriers such as grain boundaries and induce local tensile stresses which approach the material's theoretical cleavage strength.

The role of the environment on fatigue crack nucleation and propagation has not been clarified. Initial stages of slip band formation and growth occur even in vacuo, in inert atmospheres or when the metal is protected by impermeable organic coating. Latter stages of fatigue, however, appear to be affected by presence of reactive environments such as atmospheric oxygen. It has been suggested that oxygen atoms absorbed on a slip step may either prevent slip in a reverse direction on the same plane or assist oxygen atoms in entering the metal to give a plane of weakness. Oxygen atoms possibly assist in maintenance and growth of fatigue cracks by some other mechanism.

In a corrosive aqueous environment, the actual solution of metal atoms may

create also a shower of vacancies, thus determining the location of crack nucleation and propagation.

Simnad,[27] in a two stage investigation of corrosion fatigue, observed the importance of the distribution of pits upon specimen life before fracture. When the cracks become very sharp, the increase in resistance, as the crack deepens, will outweigh any further rise in emf. Eventually, therefore, propagation rate of this first crack will slow down, and other pits will begin to develop into cracks. In any event, the shape of the pits and their distribution along the surface must have a great effect upon specimen life before fracture occurs.

Reasons for the curves of Figures 6, 7 and 8 are to be found in an examination of typical test specimen surfaces shown in the photomicrographs of Figures 9 and 10. Figure 10 photomicrographs show part of longitudinal cross-sections of wires subjected to various temperatures but otherwise kept under the same conditions. Magnified 100 times and unetched, these sections show marked differences in the size, shape and distribution of pits. As the temperature increased, the pits became more numerous, more uniform and shallower.

The two photomicrographs in Figure 11 with a 500 magnification illustrate the remarkable difference in pit shape at 180 F and those at 80 F. At their base, the pits are much deeper and sharper at 80 F than they are at 180 F. This explains the definite improvement observed in corrosion fatigue properties at higher temperatures. This observation indicates that there exists an additional factor, frequently neglected, which affects the corrosion fatigue mechanism. This factor is polarization which governs distribution and type of attack under conditions of cyclic stress.

The difference in this pitting distribution may be attributed to the resistance that the film on the surface offers to oxygen diffusion. At higher temperatures, the rate of oxygen supply to the metal surface increases, and the oxygen is more uniformly distributed although its concentration in the solution is the same or even lower than at room temperature. Consequently, the metal surface is consumed more evenly along the wire without producing any stress-concentration points. At room temperature, oxygen supply to the surface has a more random distribution; thus, once attack has been
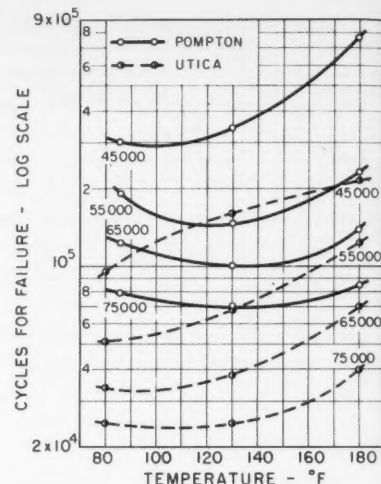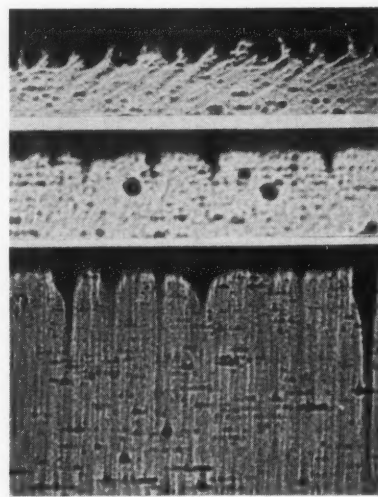

Figure 9—Effect of temperature on distribution of pitting at 45,000 psi stress. Upper section: 180 F, middle: 130 F, lower: 85 F. Unetched, 100X.

started by some local peculiarity, an aeration cell will be formed, concentrating the attack at that point. Because the neighboring areas are practically unattacked, a stress-concentration area will be formed at pit base, further deepening the pit and propagating it into a sharp crack.

Since it is known that the reaction is cathodically controlled, this effect may also be explained on the basis of the ratio of cathodic to anodic areas. At 180 F, due to the more dense and uniform pitting, ratio of cathodic to anodic areas is smaller than at room temperature; hence no sharp pits can be developed. On the other hand, at room temperature with pitting more at random, this ratio is large and accelerates deepening of existing pits. The intermediate temperature must be a case in which the pits are shallower than at 86 F and fewer than at 180 F. In a situation where the material is more notch sensitive, the inter-
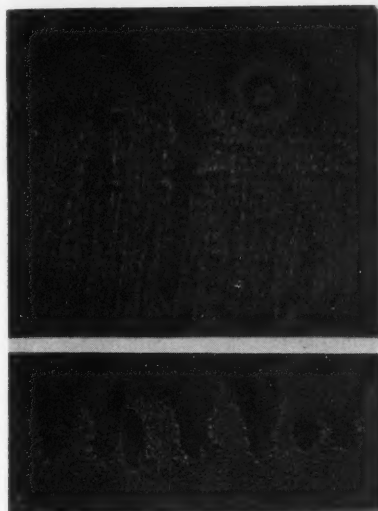
Figure 10—Comparison of pits. Top section: pitting at 80 F; bottom section: pitting at 180 F. Magnified 500X.
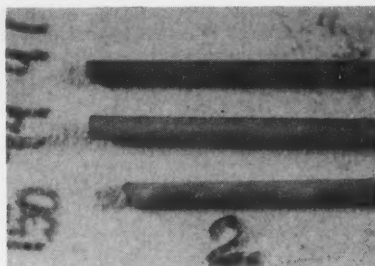

Figure 11—Comparison of three Pompton steel specimens at following conditions: Top, 180 F, 0.6 ppm O_2, 45,000 psi, 465 minutes. Middle: 130 F. 0.8 ppm O_2, 46,000 psi, 367 minutes. Bottom: 86 F, 4.8 ppm O_2, 45,000 psi, 405 minutes.
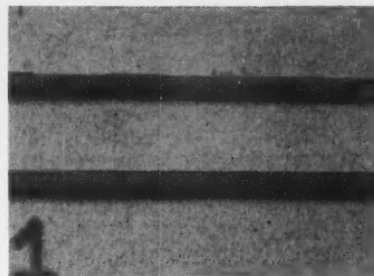

Figure 12—Comparison of two Pompton steel specimens subjected to corrosion fatigue at 180 F and 45,000 psi stress. Upper section: effect of electrolysis. Lower section: chemical attack without electrolysis.
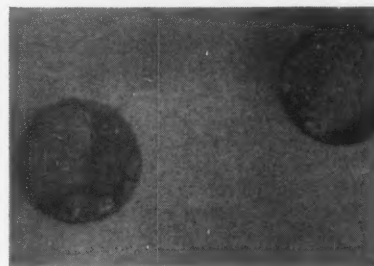

Figure 13—Typical corrosion fatigue failures. Magnified 40X.

mediate temperature type attack may be more destructive than at room temperature.

Corrosion product at all temperatures proved to be a green hydrated magnetite, which is typical for cases with limited oxygen supply as fixed by the test conditions. Corrosion product distribution was more uniform at 180 F than at 86 F, as illustrated in Figure 11. In Figure 11, although oxygen concentration was higher at room temperature by a ratio of 8 to 1, the attack at 180 F was more uniform. This fact is further evidence that the controlling link in corrosion fatigue is the film resistance to oxygen diffusion and not oxygen concentration in the solution. The Pompton wire shows a certain maximum effect as to the damage rate at approximately 130 F. The cause of this phenomenon is obscure.

Figure 12 shows the difference in corrosion between a wire that made contact with the stainless steel tank (resulting in galvanic action) and a wire under normal insulated conditions. The severe attack on the former explains the importance of insulating the specimens during tests.

Two typical corrosion fatigue failures in Figure 13 illustrate penetrative action of the solution which eventually causes the wire to break at the center.

Apparatus used in this investigation appears to be suitable for many types of corrosion fatigue studies. Such variables as temperature, circulation, concentration of solution and oxygen concentration could be controlled easily. Operation of this apparatus proved to be simple and economical, especially in regard to specimen cost. The equipment can be recommended for many qualitative studies such as the effect of different inhibitors, accelerators, various solutions and gases, and may be applicable for studying corrosiveness of different media under conditions of low oxygen concentrations and higher temperatures as encountered in most oil wells.

Conclusions

The following conclusions, based primarily on the results of this investigation, refer to the temperature effect on steel corrosion fatigue in dilute sodium chloride solution.

1. Corrosion fatigue properties at 180 F show definite improvement over those at room temperature.

2. Temperature influence on the corrosion fatigue mechanism is manifest through types of pitting attack at different temperatures.

3. The metal surface is more evenly pitted at 180 F than at 80 F. Also, the pits at 180 F are shallower and more rounded at their base.

4. Improvement in corrosion fatigue properties depends on the kind of pits developed and their distribution along the surface. This distribution causes the ratio of cathodic to anodic areas to be higher at 80 F than 180 F.

5. Raising the solution's oxygen concentration from 1.0 to 4.8 ppm at 86 F and from 1.0 to 2.8 ppm at 130 F did not affect the S-N results. Hence it is believed the controlling link in pitting attack under cyclic stressing, as affected by temperature, is the resistance of the film near the metal surface to the oxygen diffusion rate.

6. Results of this investigation differ markedly from results obtained by Gould[16] and Paul[18] on temperature influence and corrosion fatigue. The differences can be attributed to differences in experimental conditions.

7. More work on the problem is required because there are only three studies available on the influence of temperature on corrosion fatigue.

8. Apparatus used was highly versatile for corrosion fatigue tests under various conditions. It affords easy control of most variables existing in corrosion fatigue testing and is especially suitable for qualitative studies of various kinds.

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APPENDIX—1 Method of Calculation of Experimental Data

Nomenclature:

E is the modulus of elasticity, in lb/sq inch.

d is the diameter of the wire, in inches.

Θ is the angle of inclined bearing with the horizontal.

C is the horizontal chord distance from end to end of bearing (distance ab) in inches.

S is the extreme fiber stress at the surface of the wire, in lb/sq inch.

L is the length in inches of the arc between bearings.

I/c is the section modulus of the specimen for a circular specimen.

R is the radius of curvature of the wire, in inches.

M is the applied moment, in lb-inches.

ΔS is the stress correction due to the weight of the wire, in lb/sq inch.

W_1 is the weight of the specimen corrected for buoyancy in lb.

h is the horizontal distance from face of bearing to a point above the center of gravity of half the specimen, in inches.

The specimen is bent to the arc of a circle to give a uniform strain along the wire (15 to 50 cm).

For a moment applied at the ends, the curvature may be calculated from

$$\frac{1}{R} = \frac{M}{EI} \qquad (1)$$

From the beam equation, the stress on the extreme fiber is

$$S = \frac{M}{I/c} \qquad (2)$$

where $c = \frac{d}{2}$ for a wire. Hence, combining Equations 1 and 2,

$$S = \frac{E d}{2 R} \qquad (3)$$

In Figure 14, the chord C, which is easily measured, may be expressed in terms of the curvature R as follows:

$$C = 2 R \sin \Theta \qquad (4)$$

Finally, substituting for R in Equation (3),

$$S = \frac{E d \sin \Theta}{C} \qquad (5)$$

Equation (5) was the basic equation used to calculate the stress. By simple trigonometric manipulations, the stress S may also be expressed in terms of arc length L:

$$S = \frac{\pi E d \Theta}{180 L} \qquad (5a)$$

Since the modulus of elasticity, E, was assumed to be 30×16^6 psi, the diameter of the wire was 0.039 inches, and the angle of bearing inclination was 36 degrees, Equations (5) and (5a) reduce to

$$S = \frac{68.5 \times 10^4}{C} \qquad (6)$$

or

$$S = \frac{73.6 \times 10^4}{L} \qquad (6a)$$

The results plotted in Figures 4 and 5 were calculated by using either Equation (6) or (6a).

Correction for the slight increase in stress at the center of the wire, due to catenary action, may be calculated using the equation given by Paul:[17]

$$\Delta S = \frac{16 W_1 C \sin \left(\frac{\Theta}{4} \right) \cos \left(\frac{\Theta}{4} \right)}{\pi d^3 \sin \Theta} \qquad (7)$$

Again, the values for W and d are substituted and the correction expressed on a relative basis, the equation is
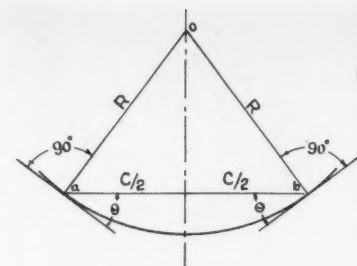
Figure 14—Use of graphic method in calculating experimental data.

$$\delta = \frac{\Delta S}{S} = 9.42 \times 10^{-6} C^3 \qquad (8)$$

where δ is the factor by which the apparent stress should be multiplied to obtain the true stress at the center of the wire. In the present investigation, this correction never exceeded 3 percent and thus was assumed negligible throughout.

Discussion by L. W. Vollmer, Gulf Research and Development Co., Pittsburgh, Pa.

1. Did straightening of wire specimens influence results?

2. Opinion: Depending on conditions, the answer to the question "Does temperature lower corrosion fatigue resistance" is yes, no or maybe?

Reply by I. Cornet:

1. Coiled wire subjected to hand straightening gives variable performance in corrosion fatigue. In the investigation reported here, drill rod was used, and this drill rod gave consistent and reproducible data.

2. It is my opinion that the answer to the question may be yes, no, or possibly, depending on the corrosion fatigue conditions prevailing.

Any discussion of this article not published above will appear in the December, 1959 issue

Erosion of Materials by Cavitation Attack*

By D. PECKNER

Introduction

THE CORROSION-EROSION of internal surfaces of components is most often associated with the phenomenon of cavitation. This paper will discuss some of the causes and effects of cavitation, the various methods available for testing for cavitation resistance and the ways in which the cavitation effect can be decreased.

Cavitation[1,2] is primarily a wearing away of metal by erosion, or abrasion resulting from repeated impact blows produced by the formation and collapse of vacancies within a fluid. If the environment is corrosive, cavitation increases the corrosion rate; because of pitting, the accelerated corrosion rate in turn increases the severity of cavitation effects. Cavitation is the final result of transient voids in a rapidly moving liquid stream, the voids forming because the liquid tends to flow in a relatively straight line rather than adjust to the irregularities and changing contour of the flow channel. This inability to adjust often results in separation, localized decreases in fluid pressure, and strong formation of eddies. If the static pressure decreases to a value below the vapor pressure of the liquid, cavities (or voids) will form.

The voids are usually considered to be at very low pressure, sometimes approaching a vacuum.[2] When the voids collapse, with high frequency and violence as they do in regions of severe cavitation damage, a hammer-like effect accompanied by considerable noise is produced on the surface of the metal. Cavitation is particularly harmful, as can be seen when the effects of a cavity collapsing against a metallic surface[1] are considered. These effects are:

1. The metal is severely deformed under repeated impact.

2. In some areas the metal may be torn away from the matrix.

3. Any corrosion-resisting film or scale previously formed on the surface is rapidly removed, allowing initial high-corrosion rates to continue unchecked. Thus, in a corrosive environment, catastrophic attack frequently takes place where cavitation is severe.

Under actual operating conditions, cavitation may manifest itself in several ways.[1] By increasing the wall roughness of a system the resistance to flow will be increased, as is evident from the form of conventional friction factor—Reynolds number plots. High noise levels and vibration may develop in the system. Irrespective of an increase in the pressure drop which causes flow, the system may develop an upper limit of flow

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About the Author

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rate. This condition is manifested by a marked decrease in pumping efficiency.

Causes of Cavitation

Since liquids cannot support tensile stresses, cavities form whenever the absolute pressure falls below the vapor pressure of the liquid. The cavity continues to grow as long as it is in a region at or below the vapor pressure and starts to collapse as the pressure becomes greater than the vapor pressure.

A cavitation parameter, K, (related to the "number of velocity heads" concept found in hydraulics) has been used[1,3] where:

$$K = \frac{(Po - Pv) \, g_C}{(\rho Vo^2) / 2}$$

where: Pv = pressure within the cavity (usually the vapor pressure)

Po = static pressure

ρ = density of the liquid

Vo = uniform flow velocity of the liquid

g_C = mass acceleration to force conversion constant

The larger the value of K, the less is the possibility of development of cavitation.

Some of the factors contributing to pressure reduction may be seen in Bernoulli's equation for a streamline in frictionless flow:

$$\frac{g_C P}{g \rho} + \frac{V^2}{2g} + Z = constant$$

Abstract

The relationship between cavitation attack and erosion of metals is discussed. Some of the causes of caviation are outlined and consideration given to possible mechanisms of cavitation attack. Methods of reducing the cavitation effect are discussed briefly as are methods developed to test resistance of materials to cavitation-erosion. Extensive references are made to existing literature on cavitation attack.

Data are reported on the effect of hardness on accelerated cavitation testing of chromium stainless steels, effect of sodium dichromate inhibitors on resistance of metals to pitting, and determination of the relative erosion resistance of alloys by the vibratory method.

It was found that streamlining, good surface finish and the use of cavitation resistant materials tended to reduce the cavitation effect. The relative resistance of metals to cavitation could be evaluated successfully with a two-hour magnetistrictive test even though no direct correlation could be made between test results and service life.   3.5.3

where: P = static pressure, ρ = density of fluid

V = fluid velocity

Z = elevation, referred to a datum

g = acceleration due to gravity

g_C = mass acceleration to force conversion constant

Since P, (inlet pressure) and density are usually not varied once a system is set up, V and Z are the controlling factors. Considering only the effect of elevation, it is evident that cavitation is more likely to appear at the top of a conduit than at the bottom. The equation also indicates that the low static pressures are encountered in a high-velocity region.

The most important factor, however, does not appear explicitly in Bernoulli's equation.[4] This is flow curvature, the effects of which are shown schematically in Figure 1. Flow in curved channels, particularly at high velocities, is invariably accompanied by separation eddies, vortices, and changes in boundary layer phenomena. Cavitation caused by pressure reduction at local flow curvatures is probably the most prevalent type encountered.

When cavities are formed by a separation from a divergent boundary they have a fairly regular formation frequency which is approximately proportional to the rate of flow and inversely proportional to the length of the cavity. A complete cycle of the formation of a cavity is shown in Figure 2. High-speed motion pictures used[5] in a study of cavitation indicated that voids caused by cavitation form vapor bubbles of the order of 0.3 inch in diameter, have a life of 0.003 second and collapse at a maximum rate of 765 feet per second upon the surface on which they form. Their calculations indicate that this rapid

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ORIFICE   ENTRANCE   VORTEX

A – LOW PRESSURE AREA

B – HIGH PRESSURE AREA

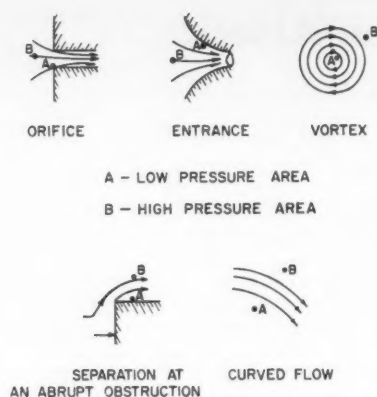SEPARATION AT   CURVED FLOW
AN ABRUPT OBSTRUCTION

Figure 1—Areas of pressure reduction under various flow conditions.

collapse produces a severe water-hammer effect, generating pressures of at least 50,000 psi on the surface of the metal.

A cavity caused by a vortex does not collapse in the manner shown in Figure 2. If the flow were perfectly steady, collapse would not occur. However, the flow is not steady and the turbulent nature of the flow causes whipping of the unattached end of the vortex. This in turn causes a small portion of the major cavity to be detached, with subsequent collapse in the regions of higher pressure.

When eddies are shed from boundary irregularities, or are caused by the mixing of jets entering a low-pressure region, the pressures at their centers may be low enough to produce a cavity which will continue to move with the flow and collapse further downstream. Other types of cavities apparently form as small bubbles, possibly starting with a tiny air bubble as a nucleus. Such bubbles have been observed to expand in a region of low pressure and disappear when they enter a region of high pressure.[4]

A bubble nucleus has been defined[6] as a bubble of such size that the thermodynamic potential of the new vapor phase is equal to that of the liquid phase. In general, the nucleus is a very tiny bubble which is at the threshold of growth. It can either grow continuously (leading to rupture of the liquid phase) or it can be redissolved into the liquid, with equal probability for both processes.

The work required[7] for nucleus formation, W_n, is given by:

$$W_n = \frac{4}{3} \pi r_n^2 \sigma = \frac{16 \pi \sigma^3}{3 (P_n - P_1)}$$

where: r_n = radius of nucleus

       σ = surface tension

       P_n = internal pressure of nucleus

       P_1 = static presure of liquid

The internal pressure is the pressure imposed upon the liquid augmented by the capillary pressure due to surface tension, i.e:

$$P_n = P_1 + \frac{2\sigma}{r_n}$$

Surface tension and the radius of the nucleus are therefore factors on which W_n is directly dependent. This work is less at an interface than it is within the liquid.

Other factors also affect W_n, e.g.:

1. As the angle of wetting of the liquid on the surface becomes smaller than 180 degrees, W_n increases. At complete wetting (0 degrees), W_n is a maximum, since the vapor phase must break the adhesive bond between the liquid and the wall.

2. W_n is larger for concave than for convex walls because of the change of strength of the adhesive forces on the surface with curvature.

3. Rough surfaces and sharp-edged intersections tend to reduce W_n, thus making establishment of a new phase easier.

4. The presence of microscopic particles within the liquid phase decreases W_n and these act as focal points about which the vapor phase may form. Occluded gases also act as focal points for nucleation.

Below the vapor pressure of a liquid $(P_1 = -\gamma_1)$, the state of a bubble is described by the equation:

$$\left[\frac{2\sigma}{r} - \gamma_1\right]\left(\frac{4}{3} \pi r^3\right) = nkT$$

When the bubble nucleus radius reaches an upper value, r_{max}, the bubble grows spontaneously without requiring further vaporization into it, until the liquid ruptures, destroying the state of tension and creating a permanent vapor phase. Solving the above equation for conditions at the maximum radius:

$$r_{max} = \frac{4}{3} \frac{\sigma}{\gamma_1}$$

The number of molecules in this maximum size bubble are given by:

$$n_{max} = \frac{128 \pi \sigma 3}{81 kT \gamma_1^2}$$

According to Bernath, the expressions for these various maximums require values of the order of 200 atmospheres for γ_1 $(-P_1)$ in ordinary liquids. Since

$$P_{max} = \frac{\gamma_1}{2},$$

the pressure within a bubble of radius r_{max} cannot exceed 100 atmospheres without causing rupture of the liquid phase and establishing a permanent vapor phase. These pressures are not those ordinarily thought of by mechanical engineers and metallurgists when considering cavitation, judging from the literature on cavitation. The bubbles dealt with here are tiny, containing 80 to several thousand water molecules.

The rate of bubble formation, J, is given by:

where: Z_1 = number of molecules per milliliter of the liquid phase

      b = pressure parameter = $\dfrac{P + \gamma_1}{P}$

      ω_1 = number of molecules flowing through the phase boundary per second per square centimeter of surface

      A = surface area of nucleus;

$$A_{max} = \frac{64 \pi \sigma^2}{9 \gamma_1^2}$$

      λ = molecular heat of vaporization

      k = Boltzmann constant

      T = °K

$$w_{max} = \frac{64 \pi \sigma^3}{27 kT \gamma_1^2}$$

Mechanisms of Cavitation Attack

The exact mechanism of cavitation-erosion is not known. Hypotheses concerning the mechanism of attack seem to be based both on logic and speculation. It is known definitely that high pressures exist in the region of collapse and most theories begin with this assumption. The existance of high pressures was demonstrated by tests at MIT[4] in which short tubes made of lead and having one end closed, were filled with water and placed with their open ends in the region of cavity collapse. The tubes were stretched quickly by the intermittent high pressure-shocks and soon failed in tension.

The action of a collapsing cavity therefore seems to be primarily mechanical, with chemical corrosion effects playing only a minor role. However, the pitting of materials by cavitation is primarily a fatigue-type of action. It is well established that metals fail in fatigue more rapidly in the presence of a corrosive medium.

Surface finish[4, 8] has a definite effect on the speed of pitting although a quantitative correlation between erosion rate and surface finish does not appear to have been developed. It has been observed however that test specimens with rough surfaces are invariably destroyed more rapidly than similar specimens with smooth surfaces. Higher stress concentrations which undoubtedly exist on rough surfaces may contribute to the reaction.

Other contributing factors regarding mechanisms of cavitation have been advanced:[4]

1. On a very rough or cracked surface, it is possible for highly compressed cavities to be driven into a fissure on the material followed by explosion of these cavities when the pressure drops in the surrounding region.

2. Spaces at the inner ends of cracks in the material act as cavities them-

$$J dt = Z_1 \omega_1 A_{max}{}^{ln}\left(\frac{b-1}{2}\right) e - \frac{\lambda}{kt} \quad e^{\dfrac{-w_{max}}{kt}}\left[1 + 2/3 \ln \frac{(b-1)}{2}\right] dt$$
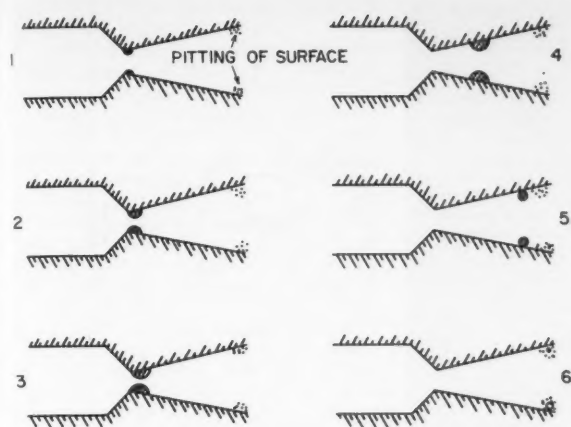
Figure 2—Complete cycle of the formation of cavitation showing the collapse of a single cavity.
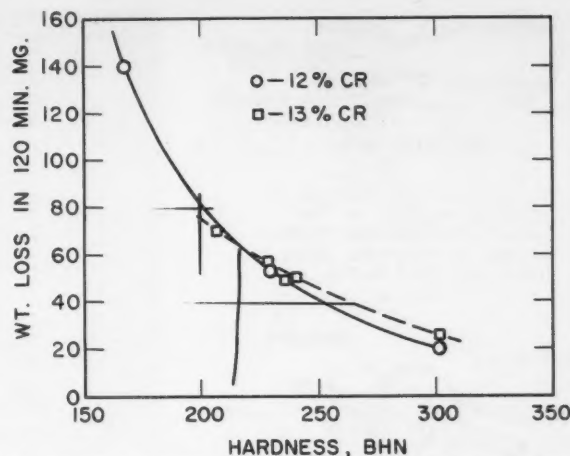
Figure 3—Effect of hardness on accelerated cavitation testing of chromium steels.

TABLE 1—Effect of Hardness on Accelerated Cavitation Testing of Chromium Stainless Steels

Specimen	Material		Rate of Loss, mg/minute During Last 30 Minutes of Test	Total Loss in mg in 120 Minutes
	% Cr	BHN		
1	12	302	0.20	20
2	13	302	0.26	25
3	13	235	0.43	49
4	13	241	0.39	51
5	12	225	0.55	54
6	13	229	0.46	57
7	13	207	0.51	70
8	12	167	0.73	141

Cited from: Reference 8

selves and collapse with explosive force when local pressures at their outer ends are increased by cavities collapsing in the flow.

3. High pressure at the inner end of a fissure is generated by the reflection of a pressure wave entering the fissure.

It would appear that cavitation is almost a self-generating mechanism of destruction. No matter how smooth a surface finish may be, once cavitation attack begins, conditions are immediately created for an increased rate of attack.

The mechanical properties of the material under study must also be considered in assessing cavitation-erosion damage. If the metal undergoes elastic deformation before acquiring a permanent set and if the water impact is greater than that required to deform it, surface hardening occurs until the limit of work hardening is reached and the metal begins to disintegrate. This is typical of the behavior of soft metals, which frequently give good service.

If the metal undergoes elastic deformation before acquiring a permanent set and if the intensity of the water blow is less than that required for plastic deformation the metal may fail in fatigue. Such metals are most suitable for resisting cavitation-erosion in high-pressure water systems.

In the case of hard, brittle materials, when the pressure of water impact exceeds that of the hardness of the metal (expressed as a comparable load per unit area) the metal disintegrates.

The indication is that many factors must be considered in determining re-

sistance to cavitation-erosion.[10] The yield point, capacity for deformation or energy absorption, tensile strength, fatigue properties, original hardness, grain size, grain shape, distribution of alloy constituents, chemical composition, impurities, and crystallographic properties all take on some measure of importance.

The degree to which these properties must be examined in assessing potential for resistance to cavitation cannot be stated quantitatively. However, the yield point, tensile strength, capacity for deformation and the fatigue limit may be termed primary influences. The remaining, or secondary influences, are in this latter category only because they do not change the gross nature of the failure.

One author[11] suggests that damage due to cavitation-erosion is not the result of bubble collapse. This hypothesis is based upon analogies rather than on experimental results. The author assumes that the bubble can not collapse, but rather is compressed to a minimum finite radius leading to development of local transitory high-temperature regions. By assuming that the bubble is filled with water vapor and assuming also there is no heat loss during compression, then in this particular case (temperature 74 degrees F, water vapor pressure 0.2 psia) the pressure of the water vapor at minimum radius is 2830 psi and the temperature is 2043 degrees F. Compressing such high-temperature, high-pressure bubbles against the metal surface would heat the surface locally and more easily allow plastic flow to occur. Any application of pressure at these elevated

temperatures would be certain to cause some damage. Gross damage is pictured as being an accumulation of defects resulting from many of these microscopic hot spots.

Other workers have also speculated that a bubble which is compressed, rather than collapsed, can reach extremely high value of temperature and pressure. In one case, Harrison[12] found that for a bubble having an initial radius of 1 cm, the maximum pressure at the bubble is approximately 4000 atm. Others[13] have estimated that a bubble, collapsed adiabatically in a liquid at room temperature, with a static pressure of 1 atm, and an internal bubble pressure on the order of 0.01 atm, would reach an internal temperature of 10,000 C.

It has been stated[9] that the magnitude of stress generated by a collapsing bubble is independent of the size of the bubble and is a function of the ratio of final to original diameter of the cavity. The magnitude of this effect is shown below:

Ratio of Final to Original Diameter	Impact Stress, tons/sq. inch
1	0
0.5	2.02
0.2	8.5
0.1	24.2
0.05	68.2
0.01	765.0

Reducing the Cavitation Effect

Two general rules can be stated concerning resistance to cavitation:

1. To have a high resistance to cavitation erosion in any particular medium, a metal should also have high resistance to the corrosive action of that medium.

2. The metal must be hard enough to offer strong resistance to mechanical attack.

Although both factors are important, there is, as yet, no direct correlation between resistance to erosion and either factor.

Erosion is primarily a mechanical attack which can be aggravated by corrosion. From another point of view, if the metal were completely resistant to erosion, but tended to corrode in the

HIGH VELOCITY LIQUID FLOW

PROJECTION CAUSING CAVITATION
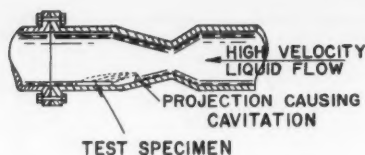
TEST SPECIMEN

THE VENTURI TEST METHOD. AN OBSTACLE PLACED IN THE THROAT OF A VENTURI TUBE CAUSES A CAVITATION ZONE OVER THE TEST PLATE.
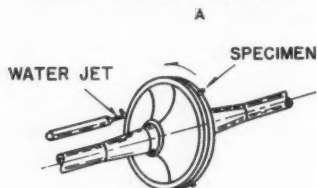
A

WATER JET   SPECIMEN

THE JET IMPACT TEST METHOD RAPIDLY ROTATING WHEEL CARRIES SPECIMEN THROUGH LIQUID JET. RESULTING EROSION IS NOT ENTIRELY CAUSED BY CAVITATION.

B

Figure 4—(a) The Venturi test method. An obstacle placed in the throat of a venturi tube creates a cavitation zone over the test plate.

(b) The jet impact test method. Rapidly rotating wheel carries specimen through liquid jet. Resulting erosion is not entirely caused by cavitation.

presence of some liquid the roughening of the surface would tend to decrease resistance to cavitation as noted in the section on "Mechanisms of Cavitation Attack."

In alloys of any particular class, where the resistance to corrosion could be expected to be similar, there is a roughly linear relationship between hardness and resistance to erosion. This is shown in Table 1 and Figure 3, using the data of Rheingans.[8]

Metallographic examination[10] indicated that failures fall into two categories. In the first, failure is due to successive deformations in the zones of highest stress concentration after the capacity to yield has been exceeded. In the second category, failure is attributed to fatigue failure beneath the zone of possible yielding where some stress distribution had already taken place.

These statements suggest several metallurgical approaches to the problem of reducing cavitation erosion. In the first case, an austenitic material (such as the 300-series of stainless steels) would in all likelihood give better service than the martensitic types (400-series) because of the greater amount of cold work which can be performed on the austenitic material.

From the point of view of resisting fatigue failures, material should be fine-grained rather than coarse-grained.[14] The fine-grained metal has a greater capacity for energy absorption before failure and, since cavitation resistance depends on ability to absorb energy, it follows that the finer the grain size, the greater the resistance to cavitation erosion. Also,
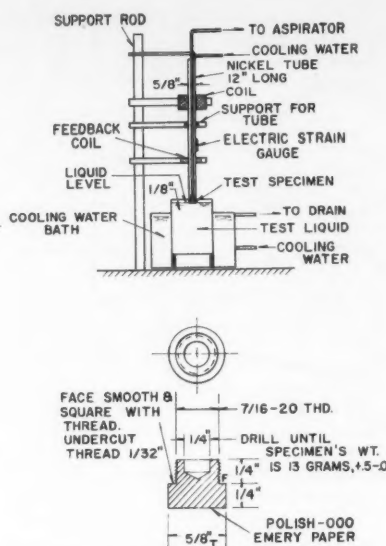
progress of fatigue cracking is retarded somewhat by a grain boundary. The more grain boundaries present, the more difficult it becomes for a fatigue crack to gain headway.

The effects of sudden changes in curvature have already been noted in Figure 1. Consequently, the fluid flow path should be as streamlined as possible in order to reduce pressure differentials which may cause cavitation.[2]

Chemically, the rate of corrosion ordinarily is greatly increased by the presence of excess dissolved oxygen. The oxygen has the effect of "depolarizing" hydrogen ions which may have been absorbed in cathodic areas, causing corrosion rates to continue at a high level. On the other hand, injection of air near points of cavitation damage has been found to decrease cavitation erosion.[15] The action of air is probably to decrease the rate of collapse of the bubbles: in effect, to provide a "cushion" against impact.

The use of inhibitors may be of some value.[8, 16] Vibratory tests (which are described in the next section) on various materials in both distilled water and distilled water with various additions of sodium dichromate gave mixed results, as shown in Table 2.

Cavitation Testing

Several methods have been developed to test resistance of materials to cavitation-erosion.[5, 8, 17, 18, 19] Unfortunately, none of the tests have been correlated with service life. Comparison of the results of the various tests does indicate, however, that material tested will be ranked in the same order of merit, although not necessarily with the same quantitative ratios of resistance as measured by weight loss.

The test most commonly used[17, 18] in previous years is one in which the specimens are placed on the expansion side of a venturi throat. A cavitation zone is
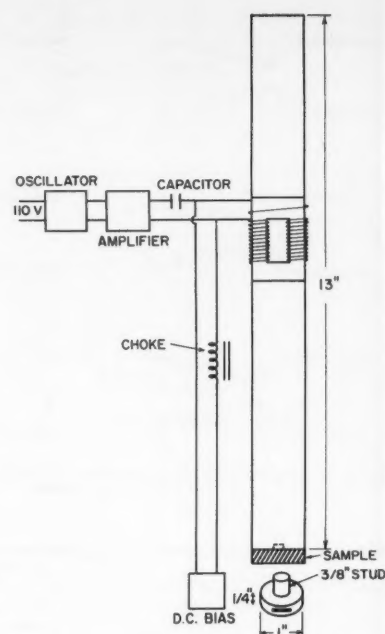
SUPPORT ROD

TO ASPIRATOR
COOLING WATER
NICKEL TUBE
12" LONG
5/8"   COIL
SUPPORT FOR TUBE
FEEDBACK COIL
ELECTRIC STRAIN GAUGE
LIQUID LEVEL
1/8"   TEST SPECIMEN
COOLING WATER BATH
TO DRAIN
TEST LIQUID
COOLING WATER

FACE SMOOTH & SQUARE WITH THREAD. UNDERCUT THREAD 1/32"
7/16-20 THD.
1/4"   DRILL UNTIL SPECIMEN'S WT. IS 13 GRAMS, +.5-0
1/4"
1/4"
5/8"   POLISH-000 EMERY PAPER

Figure 5—Vibratory-type of accelerated cavitation machine and test specimen.

produced by an obstruction in the throat and the specimen is placed in this zone. This method is the most representative of actual conditions in a hydraulic system but the time required to obtain test data acts as a strong deterrent to its use. The test setup is shown schematically in Figure 4a.

In another type of test,[17] specimens are mounted on the periphery of a rapidly rotating disc and are repeatedly carried at high speed through a jet of water. The disc rotates at 100 — 250 fps. The limitation of this test is that damage may not be produced in quite the same manner as normal cavitation-erosion because of the initial impact between the water jet and the specimen. A typical test setup is shown schematically in Figure 4b.

The third method of testing[5, 8, 17] is a magnetostrictive type in which the test specimen is rapidly vibrated in a vertical direction in the corrosive medium. When the specimen is moving in an upward direction, the pressure at the test face is greatly reduced, allowing bubbles to form. On the downward stroke, the pressure is greatly increased, causing the bubbles to compress and collapse. This cycle, which is very rapid, produces a highly accelerated cavitation test.

The test specimen is a small cylindrical plug which is screwed into the end of a nickel tube. The tube is mounted vertically and is supported by a rubber bushing at the center. Around the tube are three coils—the lowest coil is supplied with direct current to magnetize the tube and bring it into the range where it has the greatest magnetostrictive sensitivity. The middle coil is supplied with high-frequency current from a valve oscillator. This is turned to the natural frequency of vibration of the tube. The top coil provides feedback onto the grid of the valve to maintain the oscillations.

OSCILLATOR   CAPACITOR
110 V
AMPLIFIER
13"
CHOKE
SAMPLE
3/8" STUD
D.C. BIAS
1/4"
1"

Figure 6—Schematic diagram of transducer-accelerated cavitation tester.

Both the test setup and the test specimen are shown in Figure 5.

Tests have usually been run either in distilled water or sea water, although there is no restriction on the type of test medium which may be used. The nickel rod is positioned so that the test specimen is slightly under the surface of a constant-temperature bath of the test medium.

The test has been standardized so that samples are vibrated at a frequency of 6500 cps with an amplitude of 0.00324 inch. Under these conditions a velocity of 5.8 fps is obtained, as computed from the sinewave formula $V = \pi FA$ (where $V =$ maximum velocity, $F =$ frequency and $A =$ amplitude). However, at an amplitude of 0.000324 inch, the test specimen reaches a maximum acceleration of approximately 235,000 ft/(sec).[2] It is felt that the acceleration, not the velocity, is responsible for development of accelerated cavitation.

An example of results obtained in the magnetostrictive test can be found in Table 3. It should be noted that this test is performed in two hours, a decided advantage when many materials must be evaluated. This short test period is actually a necessary condition of testing because the damage is severe. Since the specimens are small, erosion is rapid, and the weight loss can be accurately determined.

One disadvantage encountered in using the magnetostrictive tester shown in Figure 5, is the generation of heat because of eddy currents set up in the nickel tube. The eddy current effect can be greatly diminished by machining two slits on opposite sides of the tube. This apparently was not done on the tester shown in Figure 5 since arrangements are made to cool the tube with circulating water.

Another type of magnetostrictive tester as shown in Figures 6 and 7 was designed by Mr. J. McDonald of the Magnetic Application Section, Materials Engineering Departments. The device consists of a transducer brazed to a connecting bar, at the bottom of which is located the sample to be tested. The sample used is similar to, but slightly larger, than that shown in Figure 5. The use of the transducer and bar decrease the problem of heat generation and allow a much more efficient utilization of power supplied to the tester. This apparatus is used in the same manner as the magnetostrictive tester noted in the literature.

Of the three test methods discussed up to this point, it is apparent that the magnetostrictive test is the most severe. Therefore, results obtained on this test may be used with confidence on the reasonable assumption that years of attack under the most severe service conditions have been duplicated. In general it can also be assumed that a good alloy will be even better in relation to a poor alloy than the test indicates. It is to be noticed that because the sample itself is part of the dynamic system, the weight loss is that for cavitation under dynamic stress conditions. It is expected that damage will be more severe than for stationary samples placed in a cavitation

Figure 7—Transducer-accelerated cavitation tester. Note the cavitation attack on the disc sample on the base of the apparatus. The cover has been removed to show the top of the transducer and cooling coil.
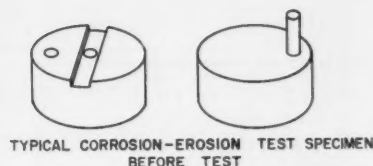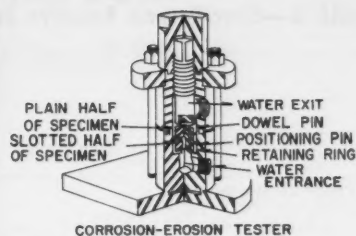
field immediately below the oscillating plunger.

A fourth test[19] has been developed recently which seems to hold some promise of good correlation with service life. Actual operating conditions with respect to temperature, pressure and circulating fluid can be easily duplicated as shown in Figure 8. Essentially, two small discs, into one of which a hole and channel has been machined, are pressed together and the test fluid is circulated through the hole. Upon hitting the blank disc, the fluid is forced to change direction. This is a stagnation point and a region of high static pressure in which any bubbles present will tend to collapse or compress. Impact and formation of eddies are also involved. The test is run for 500 hours and the specimens are weighed at the end of the test. Once again, weight loss is claimed to be the criterion for judging resistance to cavitation. The principal disadvantage of this test is the time involved in running. The test setup is not simple and actually is not truly a cavitation test.

CORROSION-EROSION TESTER

TYPICAL CORROSION-EROSION TEST SPECIMEN BEFORE TEST

A,B,J —STOP VALVES
C—FILTER
D—RECORDING PRESSURE-REGULATING VALVE
E—THERMOMETER WELL
F—THROTTLING VALVES
G—INDICATING PRESSURE GAGES
H—CORROSION-EROSION TESTERS
I—RECORDING PRESSURE GAGE
TEST SETUP
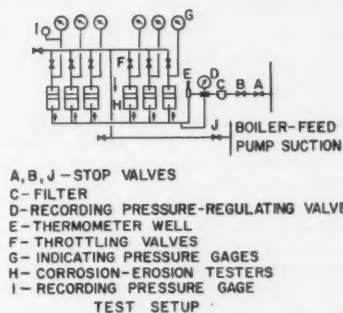
Figure 8—Sectional view and schematic diagram of corrosion-erosion test setup.

Discussion

Of necessity, statements made relating to the phenomenon of cavitation and subsequent erosion have been of a general nature. The literature indicates clearly that while cavitation has been the subject of an ever-increasing amount of research over the past 60 years, only the effects have been clearly stated. Some causes and preventative measures are generally known, but no quantitative re-

TABLE 2—Effect of Inhibitor in Test Liquid on Resistance to Pitting

Material	Test Liquid	Rate of Loss in mg/min During Last 30 Minutes of Test	Total Loss in mg in 120 Minutes
Low alloy grey iron, as cast, Hardness......Rockwell A55..........	Distilled water	0.60	68
Low alloy grey iron, as cast, RA55......	99.8% H_2O + 0.2% Chromate	0.57	67
Low alloy grey iron, as cast, RA55......	99.6% H_2O + 0.4% Chromate	0.55	67
Low alloy grey iron, heat treated, RA71.	Distilled H_2O	0.67	59
Low alloy grey iron, heat treated, RA71.	99.8% H_2O + 0.2% Chromate	0.36	36
Low alloy grey iron, heat treated, RA71.	99.5% H_2O + 0.5% Chromate	0.32	31
Type No. 1 Ni-Resist, RA43..........	Distilled H_2O	0.58	136
Type No. 1 Ni-Resist, RA43..........	99.8% H_2O + 0.2% Chromate	0.53	115
Type No. 1 Ni-Resist, RA43..........	99.6% H_2O + 0.4% Chromate	0.79	122
Type No. 2 Ni-Resist, RA43..........	Distilled H_2O	1.03	166
Type No. 2 Ni-Resist, RA43..........	99.8% H_2O + 0.2% Chromate	0.99	166
Type No. 2 Ni-Resist, RA43..........	99.6% H_2O + 0.4% Chromate	1.02	181
Type No. 3 Ni-Resist, RA42..........	Distilled H_2O	1.00	133
Type No. 3 Ni-Resist, RA42..........	99.8% H_2O + 0.2% Chromate	0.89	130
Type No. 3 Ni-Resist, RA42..........	99.6% H_2O + 0.4% Chromate	0.79	115

Note: In all sodium dichromate (Na_3CrO_4) and distilled water solutions, pH = 8.6
Cited from: Reference 8

TABLE 3—Specific and Relative Erosion Resistance of Alloys as Determined by the Vibratory Method

ALLOY	BHN	Proof Stress, kips	Max. Stress, kips	% Elong	WEIGHT LOSS BY EROSION, MG.				MERIT FIGURE RELATIVE* TO ADMIRALTY BRONZE	
					Sea Water		Distilled Water			
					First 30 min.	Next 60 min.	First 30 min.	Next 60 min.	Sea Water	Distilled Water
Cast High Tensile Brasses:										
1) Admiralty Mn Bronze	156	39.4	80.3	27	5.9	18.9	4.6	16.2	1.0	1.0
2) 5 Ni, 10 Zn, 5 Al, 1 Mn, 1 Fe, Bal. Cu	101	39.6	88.8	28	3.	9.5	...	...	2.	...
3) 5.9 Ni, 20.7 Zn, 2.6 Al, 1.8 Mn, 1.6 Fe, 0.55 Sn, Bal. Cu	145	38.	86.	18	2.5	11.2	...	...	1.7	...
Cast Monels:										
4) Normal Monel	139	37.1	83.2	35	3.7	13.4	3.2	13.6	1.4	1.2
5) 3 Si Monel	226	70.9	109.5	12	2.2	8.65	...	...	2.2	...
6) 3 Al Monel	215	76.	117.8	34	1.7	8.15	...	...	2.3	...
Cast Irons and Cast Stainless Steels:										
7) 18/2 Stainless steel as cast	236	...	....	..	2.	7.	2.	6.6	2.7	2.45
8) 18/2 Stainless steel, 1 hr. @ 1730 F, A.C., 2 hr. @ 1020 F, A.C.	273	...	....	..	1.	3.3	1.2	3.8	5.7	4.25
9) 18/8 Stainless, as cast	168	...	....	..	0.4	2.8	0.6	2.6	6.75	6.25
10) Grey Cast Iron, 3.46 TC, 1.61 Si, 0.86 Mn, 0.67 P	214	...	29.5	..	25.9	46.9	19.1	30.2	0.4	0.54
11) Ni-Resist, 3.46 TC, 1.80 Si, 0.62 Mn, 0.07 P, 14 Ni, 3.4 Cr, 6.4 Cu	179	...	32.7	..	4.4	15.5	2.3	5.8	1.20	2.80

* Merit Figure = $\dfrac{\text{Wt. lost by Admiralty Bronze}}{\text{Wt. lost by alloy}}$ A.C. = Air Cooled

Cited from: Reference 17

lationship has been derived to express them. Streamlining, good surface finish, and cavitation resistant materials are the methods for reducing the cavitation effect. How much streamlining is necessary or what range of surface roughness in microinches is necessary to raise the threshold of cavitation cannot be stated.

Testing for resistance to cavitation has progressed steadily to the point where a two-hour test may be used to evaluate relative resistance to cavitation. Even here no direct correlation can be made between test results and service life. The results of the two hour magnetostrictive test do, however, seem to be borne out under service conditions. Materials, as rated by the magnetostrictive test, will perform in a similar manner in service. The severity of the test leads to the conclusion that performance in service will be superior to results indicated in accelerated testing.

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Any discussion of this article not published above will appear in the December, 1959 issue

Acetylenic Alcohol-Inhibited Pickling Bath
As a Pretreatment Prior to Lining Steel Pipe*

By K. N. EDWARDS,[1] L. J. NOWACKI[2] and E. R. MUELLER[2]

Introduction

THERE are many acetylenic alcohols and derivatives currently being used in oil-well acidizing solutions and as inhibitors in pickling operations.[1,2,3] Although other acetylenic alcohols are available, the most commonly used acetylenic alcohols probably are propargyl and butynediol. Solubility considerations and availability are the predominant limiting factors in the use of other acetylenic alcohols.

The work described in this article had its origin in an effort to establish a better surface[4] for subsequent lining of butt-welded steel pipe sections with protective organic coatings.* In essence, a possible polymerization structure was postulated which, if actually formed, would provide an organo-metal substrate to which superior anchorage of organic coatings could be achieved. The surmise proved fruitful and several avenues of exploration were pursued in order to understand better the structure and limitations of the propargyl and butynediol-modified pickling treatments. The postulated mechanism and structure are discussed in more detail later in this paper.

Advantage of Acetylenic Alcohol Modification of Pickling Baths

The acid pickling process and the use and mechanism of pickling acid inhibitors have been the subject of many articles.[5-10] However a general pattern has been established.

Approximately three to four layers of scale will form on the steel surface depending upon the heats to which the steel was subjected during its fabrication. This scale graduates from the metal surface outward in sequence of increasing oxygen content. The outer layer is, in general, richest in oxygen. The approximate formula for this layer is Fe_2O_3 with about 30 percent oxygen by weight. The bulk of the scale is located beneath the outer layer, corresponds to the formula Fe_3O_4, and contains about 28 percent oxygen. Next to the iron itself is a layer of FeO of about 22 percent oxygen. However, between the FeO and the pure iron there may be found a low-oxygen-content solid solution of iron and mixed oxides.

The outer scale layers are relatively insoluble in sulfuric acid whereas the under layers are quite soluble as is the steel itself. In pickling, it is generally

conceded that the acid solution moves through the cracks in the outer mill scale layers and attacks the inner layers of steel. The brittle, oxygen-rich outer layers of scale flake off of the steel surface as the acid undercuts through the more soluble low-oxygen-content oxides. By the time the last of the scale has been removed, especially if some of it is strongly bonded into the surface by the hot-roll pressure on an especially thick area, three undesirable effects will have been produced.

(1) A considerable amount of sound steel surface will have been dissolved, resulting in considerable economic loss as well as a badly pitted metal surface.

(2) A corresponding amount of the pickling acid will have been uselessly consumed.

(3) A certain amount of hydrogen will have entered the steel where it may or may not cause permanent damage, depending upon the type of steel and subsequent postreatment. This hydrogen embrittlement process, according to Zapffe,[11] depends upon the dissolving of atomic hydrogen into the iron crystal lattice.

Through the use of a suitable pickling inhibitor, the fresh steel surface can be passivated and the dissolving action of the acid directed primarily at the soluble oxides binding the mill scale to the pure metal.

Both propargyl alcohol and butynediol are effective inhibitors for use in pickling tanks. In addition, both propargyl alcohol and butynediol are effective inhibi-

Abstract

Test results on steel panels confirm that acetylenic alcohols when used as inhibitors in pickling baths provide a substrate which will increase the corrosion inhibition of epoxy-phenolic systems under extreme immersion conditions. It was found that this substrate under test conditions provided protection equal to or superior to that provided by lightweight zinc phosphate pretreatment. Certain postulated reactions are offered to explain this phenomenon. It is possible that the mechanism is tied in with acid and hydrogen embrittlement inhibitive properties.

Data reported include the effect of differing metal surface treatments on the corrosion-resisting properties of epoxy-phenolic coating systems, the effect of lead ion on the corrosion resistance of pickled coated panels, and results of hydrogen embrittlement bend test for acetylenic alcohol concentration. This study was conducted primarily to improve the corrosion resistance of coated steel pipe carrying hot potable water. 5.9.2

tors of acid embrittlement. In this latter respect, the propargyl alcohol is the superior material of the two.[12]

The experiment reported in Table 1 was designed to test the hypothesis that the same structure which results in the excellent corrosion inhibition and hyrogen embrittlement resistance of the propargyl alcohol pickling bath might also provide a superior substrate to which organic coatings could be bound. In this experiment, panels which were alkali cleaned and then pickled with a propargyl alcohol-modified pickling bath were compared with (1) panels pickled in uninhibited sulfuric acid, (2) solvent-cleaned panels, and (3) zinc phosphated panels. To study the action of an acetylenic alcohol addition on subsequent phosphating, a group of panels was pickled in a propargyl alcohol-inhibited

TABLE 1—The Effect of Different Metal Surface Treatments[a] on the Corrosion-Resisting Properties of Epoxy-Phenolic[b] Coating Systems (Salted-Water Immersion)

Panel No.	Surface	Rating[c] 10 Day Period	30 Day Period	60 Day Period	90 Day Period	120 Day Period	150 Day Period
CT-16	Hot rolled, solvent cleaned	8—	8—	8—	0	x	x
CL-9	Hot rolled, solvent cleaned	8—	8—	0	x	x	x
CT-47	Hot rolled, solvent cleaned	8—	8—	4	4	0	x
CT-45	Hot rolled, alkali cleaned, pickled H_2SO_4	7	7	5	5	4	4
CT-36	Hot rolled, alkali cleaned, pickled H_2SO_4	7	6	5	5	4	4
CL-24	Hot rolled, alkali cleaned, pickled H_2SO_4	7	7	5	5	4	4
CT-34	Alkali cleaned, pickled with propargyl alcohol	10—	10—	7—	6—	6—	6—
CL-27	Alkali cleaned, pickled with propargyl alcohol	10—	9+	8—	6—	6—	6—
CT-18	Alkali cleaned, pickled with propargyl alcohol	10—	9+	8—	6—	6—	6—
CL-37	Zn Phos, pickled regular	9	8	8—	6—	2	x
CT-7	Zn Phos, pickled regular	9	8+	7—	7—	4	4
CL-12	Zn Phos, pickled regular	8+	8	8—	6—	3	2
CT-30	Zn Phos, pickled with propargyl alcohol	8+	8	7+	7—	3	3
CL-14	Zn Phos, pickled with propargyl alcohol	9	8+	7—	7—	5	5
CT-5	Zn Phos, pickled with propargyl alcohol	9	8+	8—	8—	0	x

[a] Lead-lined pickling tanks.
[b] Coating of 2.0 ml thick unpigmented epoxy-phenolic baking type.
[c] Rating is based upon panel condition. 10 = perfect. 0 = complete failure.
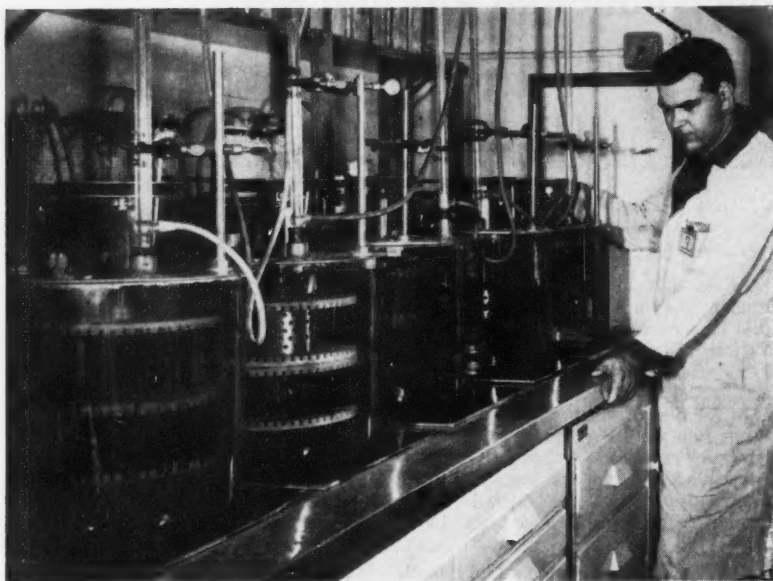
Figure 1—Corrosion cells for the evaluation of coating systems.
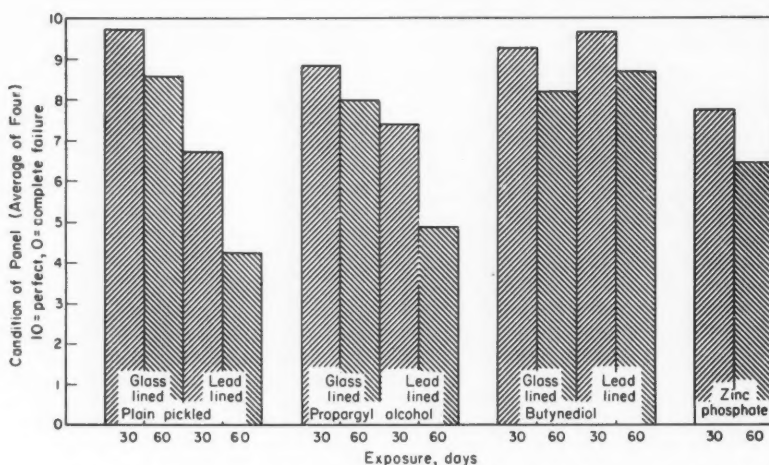
Figure 2—The effect of lead ion on the corrosion resistance of coated panels pickled in acetylenic alcohol inhibited baths. All panels were coated with 2-mil epoxy-phenolic-type coating.

pickling bath and then zinc phosphated. After pretreatment, the panels were coated with 2.0 mils of an unpigmented epoxy-phenolic baking-type coating and subjected to immersion in specially designed corrosion cells.

In these cells (see Figure 1), panels were rotated in a hot (190 F) solution of aerated distilled water to which sufficient salts had been added to bring the water just within the limits specified by the government as potable. However, no calcium salts were added. After 150 days' exposure to these accelerated corrosion conditions (Table 1), those panels pretreated with a propargyl alcohol-modified pickling operation were still in fair condition, whereas all other pretreatments were either in poor condition or had failed completely. It is interesting to note that the use of a propargyl alcohol-modified pickling bath did not

seem in any way to affect subsequent phosphating operations.

It must be noted that all of the panels evaluated in the experiment reported in Table 1 were pickled in lead-lined pickling tanks. As will be brought out later, this factor played an important part in the relative corrosion resistance of the pretreatments.

The Effect of Lead on the Corrosion Resistance of Pickled Panels

Because Wirshing and McMaster[13] had reported a detrimental effect of lead deposited on the freshly pickled steel surface from lead-lined pickling tanks, an experiment was set up to evaluate the effect of lead on the inhibitive action of propargyl alcohol and butynediol. The results of this work (reported in Figure 2) were startling. When no contaminating lead ion was present, the plain or

uninhibited pickling was a superior pretreatment for steel, as compared to a commercial zinc phosphate coating (120 milligrams per square inch coating weight). However, the addition of a slight amount of lead contaminant to the bath resulted in a considerable drop in the performance of the uninhibited pickled panels. The uninhibited pickling system, although economically not feasible, was an effective standard upon which to base performance of acetylenic alcohol inhibitors.

The propargyl alcohol-pickled panels were also adversely affected by the presence of contaminating lead in the bath, but not to the same degree as were the uninhibited pickled panels. The addition of butynediol to the pickling bath as an inhibitor resulted in a surface which was superior in corrosion resistance to that of propargyl alcohol. Surprisingly enough, butynediol became even more outstanding when lead was present in the pickling tank. In glass-lined pickling baths, the uninhibited pickling, propargyl alcohol-inhibited pickling, and butynediol-inhibited pickling all showed corrosion-resistant properties superior to those obtained from lightweight commercial zinc phosphate pretreatment.

Under conditions where the steel is to be pretreated in lead-lined pickling tanks, the use of butynediol should result in a superior metal surface for subsequent coating. However, although butynediol is slightly superior to propargyl alcohol in the development of corrosion-resistant metal surfaces, propargyl alcohol showed slightly superior hydrogen embrittlement inhibition and should be used where hydrogen embrittlement is an important factor.

It should be noted that the coating used in the experiment illustrated in Figure 2 was designed for relatively rapid failure under the corrosion cell conditions. When high-quality, corrosion-resistant finishes are used, the comparative results should more closely approximate those of Table 1. The action of propargyl alcohol and butynediol in pickling baths which had been contaminated with lead presented a clue as to the structure of the inhibiting film.

Possible Structure of the Metal-Alcohol Coating

At present, propargyl alcohol and butynediol are manufactured under high pressure using a copper catalyst following the known Reppe procedure. By reaction of acetylene with formaldehyde, both propargyl alcohol and butynediol are formed as below:

$$2 \ HC \equiv CH + 3 \ CH_2O \xrightarrow[Cn]{Ag} \rightarrow HC \equiv$$

$$CCH_2OH + HOCH_2C \equiv CCH_2OH$$

Propargyl   Butynediol
Alcohol
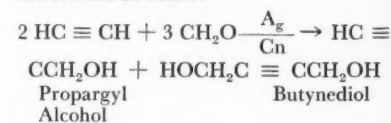
The ratio of the monohydric to the dihydric alcohol can be varied to some extent but at present it is about one part of monohydric to 15-20 parts of the dihydric component.

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marily by the work of Machu,[14] that useful inhibitors work by forming an absorbed film on the surface of the metal or at least polymerize *in situ* in some manner. The film is structurally of such a nature that monatomic hydrogen is partially prevented from entering the iron lattice while, at the same time, the freshly exposed iron is passivated to further acid attack with a resultant elimination of undue metal loss. It should be noted that all inhibitors which tend to passivate the iron surface do not necessarily form a structure capable of preventing hydrogen embrittlement.

At present, nothing is known of the actual mechanism of the elimination of hydrogen embrittlement by propargyl alcohol. Of course, it is possible that the alcohol is merely reduced by the evolved hydrogen. Nevertheless, it appeared more plausible to consider the possible polymerization of this alcohol; and if polymerization were occurring, one would expect to secure a different adhesion to organic coating materials. Both compounds are highly functional. Therefore, the type of organo-metallic bond which might be formed cannot be overlooked.

When added to the pickling bath in the proper proportions,[12] the propargyl alcohol or butynediol probably reacts at the metal surface in one of three ways: (a) reaction of the metal with the acid acetylide to form a metallic acetylide, (b) polymerization through the acetylenic bonds, or (c) the addition of the alcohol across the acetylenic bond.

Perhaps the simplest reaction of the acetylenic alcohol would be to form a metallic acetylide with the metal.

$$\text{Metal-}C \equiv C\text{-}CH_2OH \qquad (1)$$
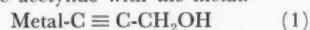
If the above reaction took place, one would expect major differences between propargyl alcohol and butynediol. According to this hypothesis, propargyl should prove effective in forming a metallic acetylide, whereas butynediol would be ineffective. Furthermore, if metallic acetylides are formed, then there should probably be no positive or detrimental effects from the addition of lead to a propargyl alcohol-inhibited pickling bath. That there were, in fact, different effects is readily apparent from Figure 2. Furthermore, Pb should react with the propargyl alcohol in much the same way as the Fe ion at the freshly cleaned metal surface. Therefore, should metallic acetylides be formed, the addition of lead to the pickling bath would be expected to reduce the effective concentration of the acetylenic alcohol without changing in any way the effectiveness of that portion of the acetylenic alcohol which formed an iron acetylide at the freshly cleaned iron surface. None of the above hypotheses proved to be true.

Another possibility which cannot be excluded is the direct polymerization of either propargyl alcohol or butynediol to form a polyolefin as follows:

$$C \equiv C \rightarrow \left[\begin{array}{cc} -C = C- \\ R \quad R' \end{array} \right]_n \qquad (2)$$
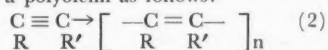
In this connection it is known that the higher polymers of acetylene forms complexes with metals. Cuprene is a good

example. However, although cuprene has been known for a long period of time, there is no definite evidence of its structure. It is known that various metals such as copper, nickel, and iron are somehow coordinated and chelated with the polymer. Some comparable reaction may occur with acetylenic alcohols.

Still another possibility is the reaction of the acetylenic alcohol to form an unsaturated polyether.

$$\begin{array}{c} R \\ C \equiv C \text{—} CH_2OH \rightarrow \\ \left[\begin{array}{c} R \\ \text{—}C = CH \text{—} CH_2 \text{—} O \text{—} \end{array} \right]_n \end{array} \qquad (3)$$
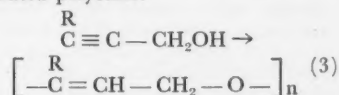
Little or nothing is known of the possible reactions of such unsaturated ethers with metals.

From both theoretical considerations and the performance of panels pretreated in acetylenic alcohol-inhibited pickling baths, one is forced to consider either that the unsaturated alcohols polymerize through the acetylenic bond as in reaction (2) or that the alcohol adds to the acetylenic linkage, yielding a polymeric unsaturated ether as in reaction (3).

It is postulated that the propargyl alcohol and butynediol polymerize into homo or heterocyclic structures on the surface of the metal, and chelate the freshly cleaned iron surface into the ring structure. If the reaction occurs in this manner, then the good adhesion of organic coatings to the prepared surface, the good resistance to hydrogen embrittlement, and the detrimental effect of lead on the corrosion resistance of the coated surface system, would be explained. The excellent adhesion of organic coatings to this structure as compared to adhesion to other inhibited structures might be explained by the tendency of the organic film to stay on the surface of the metal rather than being absorbed into the crystal lattice. If this type of thinking is true, butynediol should be expected to provide a slightly better base for organic coatings because of the presence of a greater proportion of available hydroxyl units. Such was proven to be the case. At the same time, the smaller propargyl alcohol molecule (through an alcohol-to-acetylenic bond or an acetylenic-to-acetylenic bond type of polymerization) could be expected to form a tighter structure on the surface of the metal and act as a superior hydrogen embrittlement inhibitor. Such was the case as can be seen from Table 2 and by inspection of the work done by Antara Chemicals Division.[12]

On the other hand, if lead were present in the pickling bath, it could be expected that a certain amount of this

lead would be chelated within the ring structure formed by the polymerization of either butynediol or propargyl alcohol. This chelated lead ion would tend to weaken the bond of the polymerized acetylenic alcohol to the surface of the iron, through a reduction of the total number of polymerized alcohol to iron bonds. Although blocking of the surface to hydrogen embrittlement would not be impaired under conditions of extreme corrosivity, water vapor passing through an organic coating would have a greater opportunity to undercut the film. Butynediol which has more methylol groups available for bonding to an organic coating seemed to show less susceptibility to corrosion undercutting. It is possible that the polymerized butynediol might be capable of holding and utilizing the contaminating lead as a sacrificial agent for the iron surface which it is protecting.

Laboratory Tests for Inhibitor Concentration

It was felt necessary to find some means of determining the effectiveness of the pickling bath inhibitor which would be simple enough to have practical value. Some work on the effect of propargyl alcohol on hydrogen embrittlement of steel wire in sulfuric and hydrochloric acids done by Antara Chemicals and based upon a method devised by Zapffe[11] suggested a practical answer. Because the effects of hydrogen embrittlement on the ductility of thin steel wire should be rather pronounced, samples of 1/16-inch mild steel wire were pickled in solutions of various concentrations of inhibitor with and without lead present. These wire samples were then bent 90 degrees and back until failure, and the number of cycles were recorded. A bend to 90 degrees and back to vertical was considered as one cycle. Table 2 gives the results of this test.

As can be seen, from the hydrogen embrittlement standpoint, propargyl alcohol was a far superior inhibitor to butynediol and was effective at concentrations as low as 1/2 to 1/4 of 1 percent based upon the acid present. However, for highly effective hydrogen embrittlement, a minimum of 3 to 5 percent butynediol was required. This test was found to be quite reproducible and should give a rapid indication of the condition of a given pickling bath. It must be noted that each operator will bend the wire in a different manner, and therefore, the correlation of the test will be poor from operator to operator. However, for any given operator the results

TABLE 2—Results of Hydrogen Embrittlement Bend Test[a] for Acetylenic Alcohol Concentration

Inhibitor	Concentration					
	0%	0.25%	0.5%	1.0%	3.0%	5.0%
None	3	..	..	..	..	..
Propargyl Alcohol	..	9.1	9.5	9.5	9.7	..
Propargyl Alcohol with Lead	..	9.5	9.7	9.7	9.7	..
Butynediol	..	..	7.6	9	9.6	9.6
Butynediol with Lead	..	..	7.1	8.8	9.3	9.7

[a] Average of 15 samples. Untreated wire average 9.6 90° bend cycles to failure 1/16 inch steel wire.

should be proportional to those results determined and reported in Table 2.

Summary and Conclusions

It has been shown that acetylenic alcohols when used as inhibitors in a pickling bath provide a substrate which will increase the corrosion inhibition of epoxy-phenolic systems under extreme immersion conditions. Under the test conditions encountered, this substrate provided protection equal to or better than that provided by lightweight zinc phosphate pretreatment. Certain postulated reactions have been offered to explain this phenomenon. It is very possible that the mechanism is tied in with the acid and hydrogen embrittlement inhibitive properties previously reported.

It is felt that the surface is just being scratched insofar as knowledge of acetylenic alcohol pickling mechanisms is concerned. The present interest has been primarily that of coated pipe to carry hot potable water with the work on surface pretreatment merely one aspect of the complete program. It is an aspect,

however, which will play an important role in the performance of the lining system. Therefore, in order to expand the knowledge of these materials, panels are being prepared utilizing propargyl alcohol and butynediol as well as other chemicals which, because of similarity of structure to the acetylenic alcohols, should give a good indication of the reaction at the organo-metal interface. These panels will be coated with several coatings and exposed to a series of weathering conditions. The results of these tests coupled with the work herein reported should indicate the applicability of this surface pretreatment to general preparation of steel surfaces for painting.

Acknowledgments

The authors express their appreciation to the Steel Pipe Committee of the American Iron and Steel Institute for their cooperation and sponsorship of this program, and to Dr. E. L. Kropa of Battelle Memorial Institute for his ideas and help in the preparation of this manuscript.

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Amount of Annual Purchases of Corrosion Resistant Materials by Various Industries—A Report of NACE Technical Unit Committee T-3C. Publication 59-8. Corrosion, Vol. 15, 121t (1959) Mar.

Page 122t, column 3, line 11 should read:

over 3 million dollars for special corro-

Page 122t, column 3, line 36 should read:

show that this group spent 11 million

Evaluating The Economy of Reconditioning
And Coating Underground Steel Pipe*

By GEORGE M. PEMBERTON

Introduction

THE CINCINNATI Gas & Electric Company removed, reconditioned, and reinstalled a portion of an underground 16-inch bare steel gas transmission line to compare the economy of this reconditioning program with that of replacement with new coated and wrapped steel pipe.

All underground steel gas mains installed within the past ten years were given both protective coatings and supplemental cathodic protection. The older steel mains were installed bare with time of service in some cases reaching as much as fifty years. In view of this it is hardly surprising that the various mains would have differing maintenance needs and replacement histories.

When maintenance records show that corrosion of bare steel mains is responsible for excessive repairs a basic decision must be made either to make further repairs or to renew the pipe, depending on the respective costs.

The economy of an alternate procedure, consisting of removing, reconditioning, and reinstalling the original pipe, was investigated by keeping accurate records of an actual field test installation. Results indicate that this method can, under proper circumstances, effect savings and accomplish a good installation.

Economy Study

Regardless of past expenditures for investment or maintenance, the economy study at hand should always be concerned with a comparison of present and future cost of alternate plans. Therefore, once it had been determined that the annual cost of future maintenance would exceed the annual cost of replacement with new pipe, it was proper to compare the cost of reconditioning with the cost of replacement.

It was estimated that a properly reconditioned and protected line would have a useful life approaching that of a main replaced with new pipe. As the depreciation period could be considered identical with either method, the cost comparison would comprise relative costs of reconditioning and replacement.

For the economic study, a sample job comprising 2140 feet of 30 year old 16-inch diameter by 5/16 inch wall Dresser coupled steel pipe was considered. Minimum cost of replacement with 16-inch diameter by 0.25-inch wall new pipe, complete with protective coating and cathodic protection with anodes, was es-

* A paper presented at a meeting of the Southwestern Ohio Section of the National Association of Corrosion Engineers, Cincinnati, Ohio, January 28, 1958.

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timated to be $10.00 per foot. Basis of this estimate was known costs of coated pipe and firm bids from contractors for the installation. This cost was consistent with past experience for costs of replacing sections of this line.

It was evident that the economy of reconditioning could be determined only by knowing how much of the old pipe was suitable for reconditioning and by knowing the extent and cost of spot welding required to restore the old pipe to satisfactory physical condition.

Table 1 shows a tabulation of estimated fixed costs applicable to the proj-

Abstract

By carefully selecting pipe for reconditioning, and accurately determining the time required for spot welding, the cost per foot for reconditioning an underground bare steel gas pipe line can be predicted. A method is developed to show that the economy of the total operation is related to this and other easily determined costs. A description of welding and wax coating methods used for an actual job is included with photographs, charts and graphs. 1.2.2

ect. These fixed costs appear in Table 2 as a component of the total cost per foot for various reciprocal rates of spot welding.

The cost of spot welding was determined from the contractor's actual bid of $12.50 per hour for this particular operation. Combining the constant fixed cost of $5.20 per foot with the cost of spot welding and using an overhead of 15 percent, the total reconditioning cost can be calculated as follows:

$$C = \left[\frac{12.50}{60}\right]t + .15\left[5.20 + \left(\frac{12.50}{60}\right)t\right] + 5.20$$

which reduces to the linear equation
$$C = .240t + 5.98$$

where C = total cost per foot of reconditioning

t = spot welding time in minutes per foot of pipe.

Up to this point the economy study consisted of predicting total cost of the work. It was still necessary to determine the practical field rate of spot welding that could be maintained on the job. This was done by noting the time spent on the spot welding operation. It is impor-

MIN. COST OF COMPLETE REPLACEMENT WITH NEW 16 INCH PIPE

COST OF RECONDITIONING EXISTING 16 INCH PIPE (BASED ON TIME STUDY)

COST OF WORK (DOLLARS) — vertical axis 0 to 11

SPOT WELDING TIME IN MINUTES PER FOOT OF PIPE — horizontal axis 1 to 23
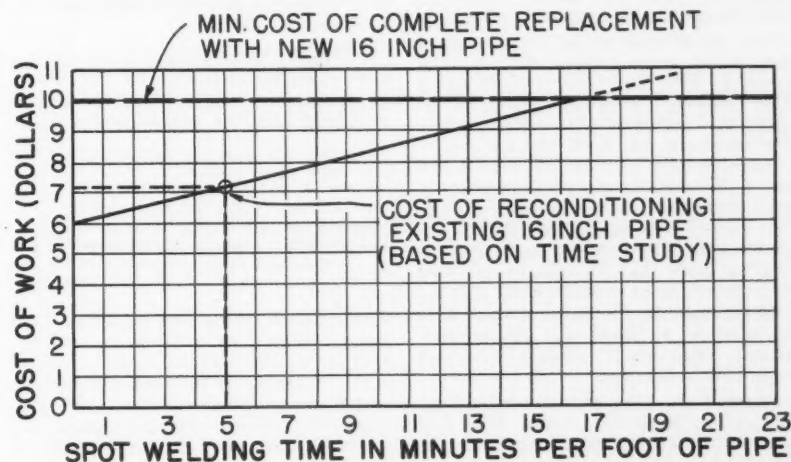
Figure 1—Estimated costs for reconditioning of old 16-inch pipe versus replacement with new 16-inch pipe.
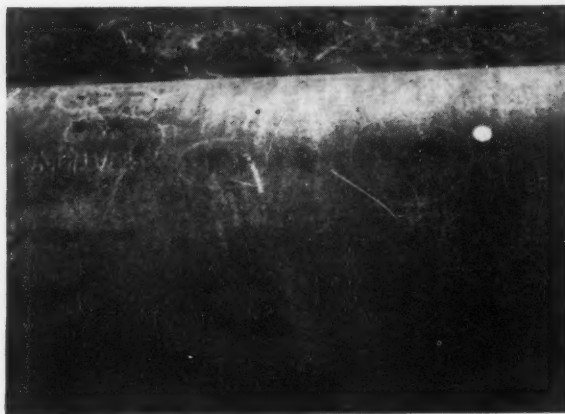
Figure 2—Close-up view of 16-inch pipe showing individual pits. Note generally good appearance of pipe surface. White spot is approximately one-inch in diameter.
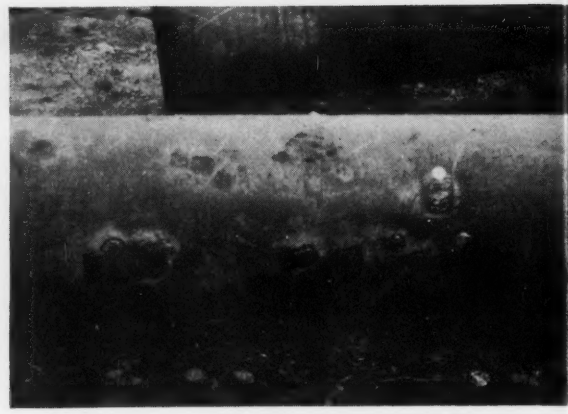
Figure 3—Close-up view of pipe section showing spot welding of pitted areas. Note 1-inch diameter reference spot.

TABLE 1—Fixed Costs Per Foot for Reconditioning 16-Inch Steel Pipe

Contract Labor:.......................... Including removal, cleaning, bevelling, testing, coating and wrapping, reinstallation, cathodic protection, and surface restoration.	$4.50
Company Labor:........................ Including inspection, disconnection, tying-in, and testing.	.40
Materials:............................ Including coatings, wrapper, and anode assemblies but excluding pipe and fittings.	.30
Total Fixed Cost Per Foot..........	$5.20

TABLE 2—Estimated Costs Per Foot for Reconditioning 16-Inch Steel Pipe

Spot Welding Time Per Foot of Pipe, Minutes	Spot Welding Cost Per Foot of Pipe, Dollars*	Fixed Cost Per Foot From Table 1, Dollars	Overhead Cost Per Foot @ 15%, Dollars	Total Cost Per Foot, Dollars
2	.42	5.20	.84	6.46
4	.83	5.20	.90	6.93
5	1.04	5.20	.93	7.17
6	1.25	5.20	.97	7.42
8	1.67	5.20	1.03	7.90
10	2.08	5.20	1.09	8.37
15	3.12	5.20	1.25	9.57
20	4.17	5.20	1.41	10.78

* Based on $12.50 hourly charge.

tant to include set-up and miscellaneous time. In other words, all the welding time billed to the company for spot welding should be included rather than just the actual arc time. The average time required for spot welding was found to be five minutes per foot of pipe, within extremes of .25 and 8 minutes per foot depending upon the number and extent of pits. The same welding operators were used for welding joints. This kept work ahead of the welding operators at most times.

Figure 1 shows the comparison of costs for reconditioning versus replacement with new pipe. For various reciprocal rates of spot welding shown on the abscissa, the reconditioning cost per foot is determined by the corresponding ordinate from the line C = .240t + 5.98 which was previously developed. Cost of replacement with new pipe is indicated by the horizontal line at $10.00 per foot.

Caution must be exercised in using Figure 1. Although it appears economical to recondition for any spot welding time of less than 17 minutes per foot of pipe, experience indicated that pipe lengths requiring more than 10 minutes per foot were deteriorated to such extent that the joints should be discarded. It was kept in mind at all times that the reconditioned pipe should compare favorably in quality to new pipe.

Table 3 shows the method used to summarize the economy of the 2140 foot project. Cost of reconditioning was established at $7.17 per foot from actual time study results of five minutes aver-

age spot welding time per foot. Note that 500 feet of pipe was discarded because of excessive corrosion and had to be replaced with new pipe. Credits at the rate of $23.00 per ton were applied for sale of the discarded pipe for use as scrap or casing. Savings of $1.68 per foot amounted to a total of $3600 in favor of the reconditioning program.

The method used in Table 3 to evaluate the economy of this particular job can be extended with accuracy to similar projects by use of the expression:

$$D = y L (R - s - C)$$ where

D = difference in cost favoring reconditioning, dollars

y = fraction of original pipe suitable for reconditioning

L = total length of project, feet

R = cost per foot for replacement with new pipe, dollars

s = salvage credit per foot, dollars

C = cost per foot for reconditioning (as explained in development of Figure 1)

For example, using this equation with data of Table 3 it can be shown concisely that D = (.766) (2140) [10.00 — 0.60 — 7.17] = $3660. As the values of both C and y can be estimated during the early stages of a reconditioning program, the economy of the program can be predicted by determining the value of D well in advance of completion of the job.

Method Used For Reconditioning

The job site was in moderately rolling terrain accessible from public roadways. The line was shut down and 20 foot single joints of pipe were removed at each end of the replacement section. This was followed by capping and blocking the line so that gas service could be maintained in all of the line except the replacement section. If backfeeding had not been possible, it would have been necessary to make an initial replacement with new pipe during a short shutdown and then recondition the pipe removed for installation during a subsequent shutdown.

Dresser coupling bolts were cut with a torch and the pipe removed one 20 foot joint at a time. Care was taken to protect the pipe ends from damage during removal and thereby reduce the need for future cutting and beveling for welding operations. Subsequent operations were conducted on the job site to avoid cost disadvantages that would be introduced by extensive hauling.

All pipe removed from the line was externally cleaned to bare metal prior to inspection. An associate engineer was given sole authority to determine which joints should be discarded and which joints should be reclaimed by spot welding. Special care and judgment was required at this stage to make sure that all pits were located and that no pipe be reused unless at least $3/16$ inch of the original $5/16$ inch pipe wall thickness either remained or could be readily re-

Figure

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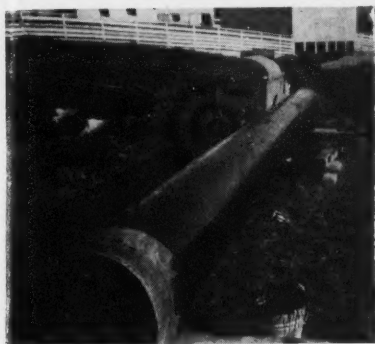
Figure 4—Length of pipe after primer applied.

Figure 6—Reconditioned joint of pipe on rollers after application of coating and wrapper.

Figure 7—Installation of reconditioned pipe in trench.

Figure 5—Application of wax coating and wrapper.

TABLE 3—Comparison of Total Cost of Reconditioning With Total Cost of Replacement With New 16-Inch Pipe

Cost of reconditioning program:	
2140 ft. pipe removed	
500 ft. pipe discarded	
1640 ft. pipe reconditioned @ $7.17	$11,800
500 ft. new C & W pipe used @ $10.00	5,000
2140 ft. program	16,800
Less salvage credit for 500 ft. @ $0.60	300
Net cost of reconditioning program	$16,500
Cost of replacement program (alternate):	
2140 ft. new C & W pipe @ $10.00	$21,400
2140 ft. old pipe salvaged @ $0.60	1,300
Net cost of replacement program	$20,100
Cost difference favoring reconditioning:	
Cost of replacement	$20,100
Cost of reconditioning	16,500
Total saving	$ 3,600
Saving per foot.....$1.68	

stored by deposition of weld metal. Each area requiring spot welding was circled as shown in Figure 2. Individual joints selected for reconditioning were found to contain from 7 to 74 such areas, the average being 37 per joint. Thirty percent of the joints were found to be in excellent condition, 25 percent were corroded excessively and had to be discarded, and the balance were moderately corroded. Had an excessive proportion of severely corroded pipe been encountered, plans for reconditioning would have been abandoned.

Each pitted area to be built up was further cleaned with a power driven wire cup brush. Weld metal was deposited over the marked areas as shown in Figure 3. Sharp projections were eliminated by grinding so that they would not penetrate into the coating. Each joint was then subjected to a hydrostatic test pressure of 300 psig to qualify for subsequent operation at 200 psig maximum working

pressure. Joints also were brushed internally.

Because both old and new pipe required field priming and coating, the coating crew could schedule their operations so as to maintain a steady work load. Each joint was primed, hot coated and wrapped by hand. Cold wax base primer was applied with 4 inch paint brushes and allowed to set up as shown in Figure 4. The pipe was supported on a pipe rolling apparatus and during hot application of microcrystalline wax, closely followed by a single wrap of 18 inch wide by .002 inch thick polyvinylidene chloride film, lapped approximately 1 inch. Coating and wrapping operations are shown in Figure 5 and a completed joint on the pipe rolling apparatus is shown in Figure 6.

Ends of the coated pipe were flame beveled where required and arc welded together along the trench. Joints were hand coated with the same materials.

Sections of the welded line were handled and lowered into the trench using canvas slings to avoid damage to the coating (see Figure 7). Seventeen-pound magnesium anodes were installed at intervals of approximately 500 feet to provide supplemental cathodic protection. Final tie-in was made using Dresser insulating couplings at each end of the replacement section.

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Ralph S. Nabors. *Gas*, 38 (1947) August.

J. A. Rupf. Socony-Vacuum Reconditions Line in Ditch Without Interrupting Service. *Oil and Gas Journal*, 51, 112, 115 (1952) November 24.

W. H. Thornhill. Spot Reconditioning Pipe Lines. *Petroleum Engineer*, 18, 228, 229 (1946) June.

NATIONAL and REGIONAL MEETINGS and SHORT COURSES

1959

Sept. 29-30, Oct. 1—Western Region Conference. Bakersfield Inn, Bakersfield, Cal.

Oct. 1-2—Southeast Region Conference. Jacksonville, Florida, Robert Meser Hotel.

Oct. 5-8—Northeast Region Conference. Lord Baltimore Hotel, Baltimore, Md.

Oct. 12-15—South Central Region Conference. Denver, Colo. Cosmopolitan Hotel.

Oct. 20-22—North Central Region Conference, Cleveland.

1960

February—Canadian Region Western Division. Vancouver.

March 14-18—16th Annual Conference and 1960 Corrosion Show. Dallas, Texas, Memorial Auditorium.

Oct. 11-14—Northeast Region Conference. Huntington, W. Va.

Oct. 19-20—North Central Region Conference. Milwaukee.

Oct. 25-28—South Central Region Conference, Mayo Hotel, Tulsa.

1961

March 13-17—17th Annual Conference and 1961 Corrosion Show, Buffalo, N. Y., Hotel Statler.

Oct. 9-10—North Central Region Conference, St. Louis, Chase Hotel.

Oct. 24-27—South Central Region Conference, Houston, Shamrock Hotel.

Oct. 30-Nov. 2—Northeast Region Conference, New York City, Hotel Statler.

1962

March 18-22—18th Annual Conference and 1962 Corrosion Show. Kansas City, Municipal Auditorium.

October 16-19—South Central Region Conference, Hilton Hotel, San Antonio, Texas.

SHORT COURSES

1959

June 2-4—Teche Section. Corrosion Control Short Course, Southwestern Louisiana Institute, Lafayette.

June 2-4—Appalachian Underground Corrosion Short Course, West Virginia University, Morgantown.

June 22-26—Massachusetts Institute of Technology Advanced Short Course in Fundamentals of Corrosion Reactions and Corrosion Control, Cambridge.

November 16-20—4th Annual General Florida Conference 1959 Corrosion Short Course. Key Biscayne Hotel, Miami.

December 7-11—University of Illinois Corrosion Control Short Course. Urbana Campus.

1960 Dallas Conference Papers Requested by Program Chairman

Technical papers for presentation at the 1960 Annual Conference in Dallas are being solicited by S. K. Coburn, chairman of the technical program.

Persons interested in submitting papers should forward titles and abstracts of papers to the appropriate symposium chairman. Names and addresses of the chairmen are given below:

Cathodic Protection: H. C. Boone, Peoples Gas, Light & Coke Co., 122 S. Michigan Ave., Room 1732, Chicago 3, Ill.

Chemical Industries: L. W. Gleekman, Wyandotte Chemicals Corp., 1609 Biddle Ave., Wyandotte, Mich.

Corrosion in the Missile Industry: Noble Ida, Martin Company, P. O. Box 179, Denver, Colo.

Corrosion Inhibitors: A. J. Freedman, Standard Oil Company of Indiana, Engineering Research Dept., 2400 New York Ave., Whiting, Ind.

Corrosion Principles: W. S. Quimby, Research and Technical Dept., Texas Company, Box 509, Beacon, N. Y.

Educational Lectures: J. L. English, Reactor Materials Section, Oak Ridge National Laboratory, P. O. Box P, Oak Ridge, Tenn.

Elevated Temperatures: D. W. McDowell, International Nickel Co., Inc., 67 Wall St., New York 5, N. Y.

General Corrosion: W. L. Mathay, Applied Research Division, U. S. Steel Corp., Box 38, Monroeville, Pa.

High Purity Water: B. G. Schultz, Westinghouse Bettis Plant, P. O. Box 1468, Pittsburgh 30, Pa.

Marine Corrosion: R. O. Norris, Cities Service Research & Development Co., Tutwiler Refinery, Lake Charles, La.

Oil and Gas: W. C. Koger, Cities Service Oil Co., Cities Service Bldg., Bartlesville, Okla.

Pipe Line—General: G. M. Jeffares, Plantation Pipe Line Co., P. O. Box 1743, Atlanta, Ga.

Plastics: J. B. Kittridge, Duriron Co., Inc., P. O. Box 1019, Dayton 1, Ohio.

Protective Coatings: R. E. Gackenbach, American Cyanamid Co., 30 Rockefeller Plaza, New York 20, N. Y.

Refining Industry: W. Janssen, General Engineering Dept., American Oil Company, P. O. Box 401, Texas, City, Texas.

Utility Industries: C. L. Mercer, P. O. Box 48, Westfield, Texas.

Deadline Dates

Abstracts of papers included on the 1960 Conference technical program must be received at the Central Office, 1061 M & M Bldg., Houston 2, Texas, by November 1. This deadline also applies to biographical sketches and photos of authors. Deadline for receipt of manuscripts is January 9, 1960.

S. K. Coburn, chairman of the 1960 technical program can be contacted at 3140 South Federal St., Chicago, Ill. Co-chairman David K. Priest can be contacted at Pfaudler-Permutit, Inc., 1000 West Avenue, Rochester 11, N. Y.

SECTION CALENDAR

May

5 Shreveport Section. Caddo Hotel.

7 West Kansas Section.

11 Central Oklahoma Section. Ponca City.

12 Baltimore-Washington Section. Ladies Night. Gannon's Restaurant, Baltimore, Md. Three films of scientific interest to ladies to be shown.

13 Los Angeles Section. Rodger Young Auditorium. Over-all Program for Marine Corrosion Control, Loren Neff of Union Oil Research.

13 Metropolitan New York Section. Shelburne Hotel, New York City. Chemical Plant Corrosion Symposium.

13 Greater Boston Section. Water Treatment, by Rolf Eliassen, MIT.

15 Ohio Valley Section. Louisville YMCA.

16 Lehigh Valley Section. Field trip through research laboratories at Carpenter Steel Company.

19 Cleveland Section. Cleveland Engineering and Scientific Center. Panel discussion led by R. Weast.

19 Chicago Section. Corrosion Problems in Water Treatment, by John R. Baylis, Chicago City Water Dept.

19 San Joaquin Section.

21 Kanawha Valley Section. Parkersburg, W. Va. Solid Plastic Materials.

21 Teche Section. Petroleum Club.

21 Detroit Section. Metallography—A Tool in Corrosion Research, by W. K. Boyd, Battelle Research Institute.

25 Atlanta Section.

26 Panhandle Section.

June

3 Teche Section. Short Course Banquet at the Petroleum Club.

5 Birmingham Section.

8 Central Oklahoma Section. Ladies Night. Tropical Cafeteria, Oklahoma City.

18 Teche Section. Regular meeting at Petroleum Club.

North Central Region News

5 Symposia Complete For 1959 Conference

Program for the 1959 North Central Region Conference to be held October 20-22 in Cleveland is being completed. Five symposia have been completed to date.

General Chairman of the conference is Les Mills of Standard Oil Company. E. W. Vereeke of Heil Process is chairman of the technical program.

The five completed symposia with the speakers to be included are given below:

Protective Linings and Coatings: "Spray Metal as a Base for Coating" by E. C. Warner, Akron Sandblast Co., "Vinyl Coatings" by C Munger, Amercoat Corporation, "Epoxy Coatings" by N. A. Mason, Pittsburgh Plate Glass, and "New Developments in Protective Linings" by Wallace Cathcart, Tank Lining Corporation.

Cathodic Protection: John Rohwedder, Corps of Engineers from Rock Island, Ill., and Art Ericson, Peoples Natural Gas Co., Pittsburgh.

Chemical Treatment: W. A. Hess, Standard Oil Company.

Materials of Construction—Metals: E. D. Verink, Jr., Aluminum Company of America, F. L. Whitney, Jr., Monsanto Chemical Co., and T. P. May, International Nickel Company.

Plastics: Otto Fenner, Monsanto Chemical Co., F. W. Arndt, Heil Process Equipment Corp., and George C. Anderson, National Tube Co.

●

Greater St. Louis Section heard C. P. Larrabee of the United States Steel Corporation speak on natural media corrosion of ferrous metals at the March 9 meeting.

The April 13 program was a talk by H. W. Penning, Douglas Fir Plywood Association, Tacoma, Wash., on the properties and advantages of plywood in the industrial market. He showed color slides of various industrial applications where corrosion is a problem.

Larry O. Goad of Larry Goad & Company has been appointed chairman of the Active Membership Committee; M. S. Van Devanter of Van Devanter Engineering Company has been appointed chairman of the Corporate Membership Committee.

Accelerated Testing of Maintenance Coatings was the topic discussed by J. W. Cushing, Carboline Company, at the April 15 meeting.

●

Detroit Section will hear W. K. Boyd of the Corrosion Research Division of Battelle Research Institute discuss "Metallography—A Tool in Corrosion Research" at the May 21 meeting.

●

Kansas City Section for its April 13 meeting heard a review of the Chicago Conference by the members who attended.

Dan Werner of American Telephone and Telegraph spoke on the application of magnetic amplifiers to cathodic protection systems at the March 9 meeting.

DETROIT SECTION heard H. P. Godard, new NACE president, present a paper on handling water in aluminum equipment at its March 20 meeting. Shown above: President Godard signing the application blank for the section's special guest, Charles Warnock (left) of Menegrande Oil Co., Venezuela. R. K. Swandby, membership chairman for the section, is shown in the center congratulating Mr. Warnock.

North Central Region annual conference dates have been set as follows: October 20-22, 1959, at Cleveland; October 19-20, 1960, at the Schroeder Hotel in Milwaukee; October 9-10, 1961, at the Chase Hotel in St. Louis.

Appalachian Short Course Scheduled for June 2-4

Over 500 registrations are expected at the Fourth Annual Appalachian Underground Corrosion Short Course to be held June 2-4 at West Virginia University, School of Mines, Mineral Industries Building, Morgantown, W. Va.

Twenty-eight new classes pertaining to underground corrosion will be offered. Thirty-three new instructors will participate in the 64 basic, intermediate and advanced corrosion classes.

Keynote address will be given by Hugh P. Godard, Aluminum Laboratories, Ltd., president of NACE. Two former NACE presidents will be included among the instructors: W. F. Fair Jr., Koppers Co., Inc., and L. L. Whiteneck, Los Angeles Harbor Department.

Complete program for the short course will be published on page 75 of the April issue of CORROSION.

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16th NACE Annual Conference and 1960 Corrosion Show will be held March 14-18 at the Memorial Auditorium, Dallas, Texas.

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Canadian Region News

CANADIAN REGION CONFERENCE COMMITTEE and Calgary Section officers, hosts to the February 11-13 meeting, are shown above left to right: G. G. Mainland of Imperial Oil Ltd., section chairman and conference technical program chairman; J. S. Watson of the government of Alberta, section program chairman and conference arrangements and entertainment chairman; L. C. Blackhall of Excelsia Refineries Ltd., conference advertising and publicity chairman; D. S. McIntosh of Britamoil Pipe Line Co., Ltd., section trustee and general conference chairman; S. N. Gell of Canadian Western National Gas Co., Ltd., section secretary-treasurer; and E. W. Abercrombie of Aluminium Company of Canada, Ltd., section vice chairman and conference finance chairman.

PANEL MEMBERS who discussed protective coatings, underground corrosion and cathodic protection at one of the Canadian Region Conference meetings in Calgary are left to right: N. T. Shideler, Pittsburgh Coke & Chemical Co., R. G. Nickells, British American Paint Co., R. M. Levy, Esso Research and Engineering Co., V. P. Milo, Shell Oil Company of Canada (chairman of the panel), J. R. Grey, B. C. Electric Co., Ltd., T. R. Stilley, Good-All Electric Mfg. Co., and W. J. Crehan, General American Transportation Corp.

264 Register for Canadian Western Division Meeting

Registered attendance was 264 at the Canadian Region Western Division Conference held in Calgary February 11-13.

Twenty papers were presented in the six symposia included on the technical program. The symposia were on corrosion fundamentals, water systems, protective coatings, underground corrosion and cathodic protection, oil and gas industries and materials of construction. Three roundtable discussions were held also.

NACE President Hugh P. Godard spoke on NACE aims and requirements at one of the conference luncheons.

The conference was directed by D. S. McIntosh, conference chairman, B. H. Levelton, Canadian Region chairman, and H. G. Burbidge, chairman-elect of the Canadian Region.

Toronto Section held a dinner meeting March 4 which featured two speakers: G. E. Beck of Interprovincial Corrosion Control Co., spoke on the use of Corrosion control instruments; T. R. B. Watson of Corrosion Service Ltd., spoke on the design of magnesium anode installations.

Western Division of the Canadian Region will hold its 1960 meeting in Vancouver, according to C. H. Townsend, consulting mechanical engineer and Vancouver Section chairman.

Edmonton Section planned a panel discussion of general corrosion problems for its March 26 meeting. Chairman of the panel was Bud Seager, Interprovincial Pipe Line Company.

how CORROSION is indexed

- By Volumes Annually in December Issue
- In NACE Bibliographic Surveys of Corrosion
- In NACE Abstract Punch Card Service
- In 10-Year Index to CORROSION
- In Engineering Index
- In Applied Science and Technology Index

$175 TO $500 PROTECTS WELL CASINGS IN HUGOTON FIELD

Galvomag magnesium anodes can prevent corrosion in gas well casings for a decade or more . . . without an external power source.

In 1954, a survey of the 6,000 odd wells in the Hugoton Gas Field revealed 56 leaks. Since most of the wells were comparatively new (two-thirds were less than five years old), this was a serious problem. Projecting the rate of leak increase showed there would be over 300 leaks by 1960.

The cost of repairing these production wasting leaks usually ran between $10,000 and $40,000, using liners or the cement squeeze method. Several Hugoton producers decided to take immediate preventative action. After extensive field tests were made, it appeared that sulfate-reducing bacteria was the villain. These microorganisms convert the sulfates into hydrogen sulphide, which in turn attacks the casings. A Dow mag-

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nesium anode distributor was asked to make an analysis of the situation and recommend a practical solution.

In determining the most practical type of corrosion protection, two factors had to be considered. First, the wells were situated a mile apart and few electric power lines were available. This meant a considerable expense if cathodic equipment requiring a power source were used. Second, to what depth would protection be possible? In some soil conditions, cathodic protection cannot be used at all. In the Williston Basin, for example, a massive layer of salt above the corroding formation blocks electrical currents from reaching this portion of the casing. Fortunately, the Hugoton field was free and clear of such obstructions.

By running potential-drop tests in casings throughout the field, it was found that a current of from 0.5 to 2.5 am-

MAGNESIUM ANODES in a wide range of sizes and shapes provide flexibility to allow the most efficient design in many different types of installations. Galvomag anodes (shown above) have 25% more throwing power than ordinary magnesium anodes . . . are used extensively in the Hugoton Field.

peres would provide ample protection to total depth. The installation of Galvomag® magnesium anodes was recommended as the best solution, from the standpoint of economy, as well as ease of installation. Also, as magnesium anodes do not set up "stray" currents in the soil, there was no danger of interference with foreign structures.

Three to eighteen anodes were used per well, at a total cost of from $150 to $500 per installation. A maximum of seven were used in each bed, about 85-100 feet away from the casing. Each well was examined individually to determine the most efficient installation. Factors such as variation in soil resistance, well-to-earth resistance and potential, and current requirements were

taken into full account in selecting the number and arrangement of anodes to be used for each well. The installations were designed for a ten year life but they may last 15 to 18 years because of polarization of the well casings.

Since 1954, over 800 wells in the Hugoton Gas Field have been cathodically protected with magnesium anodes. Casing leaks due to external corrosion are no longer a problem on these wells.

The Dow magnesium anode distributors listed below are ready to help you get the most for your corrosion protection dollar. Contact one of them next time you have a corrosion problem involving well casings, pipelines, storage tanks or other equipment.

AU-5

DOW DISTRIBUTORS provide experienced technical services on corrosion problems. Field tests of soil conditions and analyses of the requirements of individual wells can result in substantial savings in installation and anode costs.

Western Region News

Bessom

Evans

LeDuc

Mitchell

Nierman

Penner

Smith

Wilt

San Joaquin Section officers for 1959 are Chairman Jack A. Bessom, Richfield Oil Corp., Vice Chairman J. C. Chescheir, Jr., Tretolite Company of California, and Secretary-Treasurer Bruce A. Grover, Western Gulf Oil Co.

Meeting dates have been set for May 19, September 15 and November 17.

Portland Section held a panel on the corrosion problems of the pulp and paper industry at its April 9 meeting. Problems discussed included digester corrosion, dissipating generated electrical currents in a pulp beater, corrosion problems in bleached pulp washers and corrosion problems associated with liquid sulphur handling equipment. Panel members were Ed M. Read, Longview Fibre Co., Longview, Wash., W. R. Skimmin, Crown Zellerbach, Camas, Wash., Jack Decker, Columbia River Pulp & Paper Co., Vancouver, B. C., Canada, and George H. Beisse, Weyerhaeuser Pulp Division. Moderator was Dean D. Burgan, Electric Steel Foundry.

Los Angeles Section installed its 1959 officers at the March 25 meeting. They are Chairman J. I. Richardson, Amercoat Corp., Vice Chairman B. E. Black, Plicoflex, Inc., and Secretary-Treasurer Phil Burch, Lkaas Bros., Inc.

P. W. Hill and Harry J. Kipps of Signal Oil and Gas Company spoke on corrosion in the Redondo Beach (California) Field.

Loren Neff of Union Oil Research will speak on an over-all program for marine corrosion control at the May 13 meeting to be held in the Rodger Young Auditorium.

San Francisco Bay Area Section will hear Harry E. Thomas discuss the performance of electrical conductors, connectors and splices in marine environment at the May 13 meeting to be held at the Iron Duke in San Francisco.

Chairmen Selected For '59 Conference

Chairmen have been selected for the 1959 Western Region Conference scheduled for Sept. 29-Oct. 1 at the Bakersfield Inn, Bakersfield, Cal. They are:

General Conference Chairman: R. M. Evans, Standard Oil Company of Cal., Taft, Cal.

Program Chairman: J. W. Wilt, Honolulu Oil Corp., Taft.

Membership Chairman: J. A. Bessom, Richfield Oil Co., Bakersfield.

Hospitality Chairman: E. A. LeDuc, Dearborn Chemical Co., Bakersfield.

Publicity Chairman: A. J. Nierman, Standard Oil Company of Cal., Taft.

Facilities Chairman: C. J. Smith, Gulf Oil Co., Bakersfield.

Registration Chairman: J. Penner, Magna Products Co., Bakersfield.

Women's Activities Chairman: J. P. Mitchell, Jones, Keller, Inc., Bakersfield.

Technical papers to be presented in two concurrent programs will be included in the following symposia:

Corrosion in Petroleum Producing, Corrosion in Petroleum Processing, Corrosion in Chemical Processing, Corrosion in Pipe Lines, Corrosion in Utilities, Corrosion in Marine Structures and Equipment, Corrosion in Aviation Industries and General Corrosion.

Southeast Region News

Miami Short Course Dates Set for November 16-20

Tentative schedule has been made and speakers are being contacted for the 4th annual General Florida Conference 1959 Corrosion Short Course to be given November 16-20 at the Key Biscayne Hotel in Miami. The course is sponsored by the Miami Section.

The following schedule and subjects have been made, according to short course director J. B. Prime, Jr., Florida Power & Light Co., Miami:

Monday: Missiles and Aircraft.

Tuesday: Cathodic Protection Fundamentals, Rectifiers and Anodes.

Wednesday: Underground Corrosion Survey Fundamentals, Pipe Line, Lead Cable and Pipe Type Cable.

Thursday: PVC Pipe, Plastisols, Corrosion Research, Instrumentation and Non-Destructive Testing.

Friday: Coating for Corrosion Control, Chemistry of Paints, Coal Tar Coatings, Epoxy Resins, Coating Comparison and Developments.

Birmingham Section held its first quarterly meeting March 6. Herbert C. Van Nouhuys, president of Corrosion Mitiga-

Volatile corrosion inhibitors were discussed by Aaron Wachter, Shell Development Corp., Emeryville, Cal., at the April 8 meeting.

J. B. Dotson of the Pyromet Company is the section trustee.

tion Inc., and chairman of the NACE Regional Management Committee, spoke on "The Corrosion Engineer's Right Hand." He pointed out that galvanic anodes, rectifier systems, protective coatings, bonds and insulating fittings are the five fingers of the right hand for the corrosion engineer who must cope with soils of varying resistivity in protecting underground and underwater structures ranging from bare to well coated metal.

He predicted that within the next decade, cathodic protection will be specified on all new coated piping just as the past decade has resulted in the now standard practice of coating. As improved coatings are used, he stated, less cathodic protection current is required, but cathodic protection will always be economically justified as good insurance against coating flaws resulting in leaks.

Southeast Region Board of Trustees met during the recent NACE Conference in Chicago to discuss reported inactivity of most sections in the region and to make plans for the October 1-2 annual region meeting at Jacksonville, Fla.

Ohio Valley Section held its March 20 meeting in conjunction with the Louisville Electrolysis Committee. Officers elected for 1959 are Chairman Harold J. Smith, General Electric Co., Louisville, Ky., and Secretary-Treasurer John S. Heintzman, Southern Bell Telephone, Louisville.

The following meeting dates were set: May 15, Louisville YMCA, a date in August to be set later and November 20, Louisville YMCA.

Northeast Region Conference dates have been altered to add a half day. The conference dates now are October 5-8. Meetings will be held in the Lord Baltimore Hotel, Baltimore, Md.

Metropolitan New York Section will hold a symposium on chemical plant corrosion at its May 13 meeting at the Shelburne Hotel in New York City. Methods of combatting chemical industry corrosion on metals, non-metallic construction and paints will be discussed. Fundamentals on materials, temperature limitations, effect of liquid or condensate concentration, dissolved oxygen, metals versus plastics, coatings versus linings and latest experience will be reviewed. An effort will be made to show management how money can be saved and how plant maintenance improved.

Speakers for the symposium include E. G. Holmberg of International Nickel, Robert A. Pierce, Pennsalt Chemicals Corp., and Ted Hopper, Socony Paint Products Co.

A special resolution from the section was given to Fabian J. Le Febvre on February 24. He is one of the section's original members and has served as secretary-treasurer (1948-1953), vice chairman (1954) and chairman (1955). The resolution was given as an expression of gratitude prior to Mr. Le Febvre's moving to the west coast.

Greater Boston Section heard Clarence H. Sample of International Nickel's Development and Research Division discuss corrosion behavior and protective value of electrodeposited coatings at the March 11 meeting. He emphasized that efforts are being made on modifications of the almost useless salt spray test to achieve industrially useful checks on production-line results. Much of his material was drawn from ASTM Committee B-8, Programs 1 (Watts Nickel) and 4 (Bright Nickels) and from American Electroplaters Society Research Project 15 on accelerated corrosion testing. Literature on the ASTM Program 1 (zinc-cadmium comparisons and electrode-posited lead) by writing Mr. Sample at International Nickel Co., 67 Wall St., New York 5, N. Y.

Rolf Eliassen of MIT will speak on water treatment at the section's May 13 meeting.

Genesee Valley Section saw the film "Plastic Lined Pipe" at the March 31 meeting. It was presented by Paul Nobel of Republic Steel.

Southern New England Section held a discussion panel on the subject "What's New in Copper Alloys" for its April 8 meeting. Panel members were Arthur W. Tracy, American Brass Co., Waterbury, Conn., Randolph Hall, Bridgeport Brass Co., Bridgeport, Conn., and Vito F. Nole, Chase Brass Co., Waterbury, Conn.

Kanawha Valley Section will hold its May 21 meeting in Parkersburg, W. Va. Topic for the program will be solid plastic materials.

Baltimore-Washington Section will hold a special ladies night meeting May 12 at Gannon's Restaurant, Baltimore, Md. Three films of scientific interest to the ladies will be shown.

"Facilities and Techniques for Corrosion Tests of Materials Used in the Aqueous Homogeneous Reactor" was the topic discussed by H. C. Savage,

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Northeast Region News

Symposia Chairmen Selected For '59 Baltimore Conference

Birnbaum

Douty

Logan

Powell

Reinhart

Tudor

Wessel

Oak Ridge National Laboratory, at the April 14 meeting. This was a combined meeting with the Electrochemical Society, the Association of Senior Engineers of Bureau of Ships and the Washington chapter of ASME.

Symposia chairmen have been selected for the Oct. 5-8 Northeast Region Conference to be held at the Lord Baltimore Hotel in Baltimore, Md. The seven symposia and biographic data on the chairmen are given below:

Theories and Principles Symposium: Fred M. Reinhart is a supervisory materials research engineer in the corrosion section, Division of Metallurgy, National Bureau of Standards, Washington, D. C. He has been with the Bureau for 21 years. He has a BS from Juniata College and an MS from Trinity College. He is a member of ASM, ASTM and NACE. Currently he is chairman of the NACE editorial review subcommittee for Corrosion magazine.

High Temperature Corrosion: Hugh L. Logan has been associated with the National Bureau of Standards since 1936 and a member of NACE since 1953. His early work at the Bureau dealt with corrosion and stress corrosion cracking of aluminum alloys. He received a BS in chemistry from Tarkio College and a MS in physics from the University of Colorado. He is also a member of ASM, Electrochemical Society and Washington Academy of Sciences.

Corrosion in Handling Water: Sheppard T. Powell, senior partner of Sheppard T. Powell and Associates, consulting engineers, Baltimore, Md., has written technical papers and text books on water conditioning and allied problems. He received his technical education at Rensselaer Polytechnic Institute. Formerly he was on the faculty of Johns Hopkins University as an associate in sanitary engineering in the Graduate School of Hygiene. He is a member of American Water Works Association, NACE, ASME, American Chemical Society, AIChE and other organizations.

Cathodic Protection: Sidney Tudor is supervisory chemist in charge of the electrochemistry unit at the Material Laboratory, New York Naval Shipyard in Brooklyn. His experience includes research in cathodic protection, electrolytic derusting, polarography and electrochemical surface reactions. He has a BA from Brooklyn College and an MS in chemistry from New York University. He is a member of NACE and other technical organizations.

Protective Coatings: Leon Birnbaum, head of the Preservation, Decking and Insulation Section of the Navy Department's Bureau of Ships, Washington, D. C., has been engaged in corrosion work for 20 years. He has a BS in chemistry from New York City College. Specific responsibility of his section at the Bureau of Ships is protection of ship hulls against corrosion and extreme temperatures. His section also selects materials and sets insulation procedures, maintenance policies for all paints and

Symposia Chairmen—

hull coatings, electrochemical protection; decking materials and hull insulation materials.

Corrosion Inhibitors: Alfred Douty, technical director for Amchem Products, Inc., Ambler, Pa., has published papers and holds patents in the fields of protective coatings chemically formed on metals for corrosion control, additives for corrosive media and electrical control apparatus for processes. He has a BS in chemical engineering from the University of Pennsylvania and is a member of NACE, ACS, Electrochemical Society and American Electroplaters Society.

Special Corrosion Topics: Carl J. Wessel is a director of the Prevention of Deterioration Center, National Academy of Sciences, National Research Council, Washington, D. C. He has written several papers on materials deterioration and is co-editor of the book "Deterioration of Materials, Causes and Preventive Techniques." He has a BS from Canisius College, MS in organic chemistry from the University of Detroit and a PhD in biochemistry from the Catholic University of America.

Ladies Program

A ladies program is being arranged for the conference by Mrs. Doris M. Lewis, ladies committee chairman, Mrs. A. C. Burton and Mrs. John A. Hendricks.

Plans include social events for the ladies, trips to points of interest, visits to plants and an oyster roast.

Binger

Cogshall

Minor

NORTHEAST REGION OFFICERS for 1959 are Chairman W. W. Binger of Alcoa Research Laboratories, Vice Chairman A. F. Minor of American Telephone and Telegraph Company, and Secretary-Treasurer J. H. Cogshall of Pennsylvania Salt Manufacturing Company.

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Northeast Region Meeting will be held October 5-7, 1959, at Baltimore, Maryland.

E. R. P. engineers use modern methods to get design data for a pipeline cathodic protection system. This group is making current requirement tests for designing a ground bed.

South Central Region News

Teche Section Short Course June 2-4 Final Program Given

Final arrangements are being made for the Third Annual Corrosion Control Short Course to be held June 2-4 on the Southwestern Louisiana Institute campus at Lafayette. The course is sponsored by the Teche Section and the Department of Petroleum Engineering of Southwestern Louisiana Institute.

Tuesday, June 2

8:00-10:00 Registration
10:00-12:00 Introduction and Welcome
12:00- 1:00 Lunch (Student Center)
1:00- 2:00 Fundamentals of Corrosion: Jerry R. Marshall, Texas Co., Erath, La.
2:00- 3:15 Inspection for Corrosion: Dwight Evans, Engineering Testing Service, Tulsa, Okla.
3:15- 3:30 Coffee Break
3:30- 5:00 Plastic Materials for Corrosion Control: Joseph E. Rench, Napko Corp., Houston, Texas.

Wednesday, June 3

9:00-10:15 Effects of Bacteria on Corrosion of Metals.
10:15-10:30 Coffee Break
10:30-11:45 Scale
11:45- 1:00 Lunch (Student Center)
1:00- 2:15 Plastic Coatings: R. C. Booth, Plastic Applicators, Odessa, Texas.
2:15- 3:45 Corrosion Problems Offshore: R. M. Robinson, Continental Oil Co., Houston, Texas.
3:45- 4:00 Coffee Break
4:00- 5:15 Maintenance of Cathodic Protection Rectifiers: Jack C. Davis, Cathodic Protection Service, Houston, Texas.
6:30- 7:30 Social Hour
7:30   Banquet

Thursday, June 4

9:00-10:15 External Coatings.
10:15-10:30 Coffee Break
10:30-11:45 Caliper Interpretation: W. M. Kelly, Otis Engineering Corp., Dallas, Texas.
11:45- 1:00 Lunch (Student Center)
1:00- 5:00 Inhibitor Squeeze Panel: Dorsey Fincher, Tidewater Oil Co., Houston; Rupert Poetker, Sunray Mid-Continent Oil Co., Corpus Christi; and a third panel member to be given later.

Eleven topics will be included in the course: fundamentals of corrosion, inspection for corrosion, paints, effects of bacteria on corrosion of metal, scale, plastic coatings for corrosion control, corrosion problems offshore, maintenance of cathodic protection rectifiers, external coatings, caliper interpretation and inhibitor squeeze.

The registration fee of $15 includes 3 noon meals and pre-prints of some papers.

Speakers Scheduled

Some of the speakers scheduled are Jerry Marshall, Texas Co., Erath, La., Dwight Evans, Engineering Testing Service, Tulsa, Joe Rench, Napko Corp., Houston, Bob Booth, Plastic Applicators, Inc., Odessa, Tex., R. M. Robinson, Continental Oil Co., Houston, Jack G. Davis, Cathodic Protection Service, Houston, W. M. Kelly, Otis Engineering Corp., Dallas, and Rupert Poetker, Sunray Mid-Continent Oil Co., Corpus Christi.

Advanced Registration

Information and registration forms will be mailed to all NACE members in Louisiana and east and south Texas. Registration forms for non-members can be obtained from Teche Section, NACE, P. O. Box 1791, OCS, Lafayette, La.

Registration can be made in advance by mail or at the Town House Motel, Monday evening, June 1, or at Southwestern Louisiana Institute, Tuesday morning, June 2.

Committee Members

Short Course Director is John H. Selleck of Nocor Chemical Co. Other committee members include the following:

Planning and Program: John Selleck, chairman, Paul Bercegeau and Vernon Sibille.

Speakers Committee: John D. Stone, chairman, Lee R. DeRouen and Jim Alexander.

Registration Committee: Max I. Suchanek, chairman, Frank Shofner, Sam Hopson and Harry Owens.

Housing and Meals: W. A. Odom, chairman, Phil Brock and Russell Pounds.

Entertainment Committee: R. J. Cernik, chairman, and Al Prats.

Publicity Committee: Jack Donnelley, chairman.

Denver Hotels Selected For Oct. 12-15 Conference

Headquarters for the South Central Region Conference scheduled October 12-15 in Denver will be the Cosmopolitan Hotel. The Brown Palace Hotel has been selected as companion hotel. Most of the technical and symposia meetings will be held in the Cosmopolitan.

Reservations for sleeping rooms and suites at both hotels should be sent to Bryan Patterson, conference housing committee chairman, Hill Hubbell and Company, 2220 19th St., Denver, Colo.

Corporate member company requests will be honored upon receipt. Noncorporate member company requests will be dated when received and suite assignments made after September 1 in the order received until all available suits have been assigned.

Corpus Christi Section had a demonstration of the Datatron Computer for its March 24 program following the regular dinner. The computer was demonstrated by Charles A. Smith and William Bennington of Celanese Corporation.

Permian Basin Section heard J. J. Brennan, Basin Engineering Co., Midland, Tex., present a paper titled "Water Conditioning Gadgets—Fact or Fancy" by A. M. Hendricks, Hall Laboratories, at the March meeting.

Jack Ward was named as chairman of the Permian Basin Eighth Biennial Corrosion Tour.

Central Oklahoma Section will hold its May 11 meeting at Ponca City under the sponsorship of Continental Oil Company with J. D. Sudbury in charge of the program.

For its March meeting, the section heard J. P. Stanton, Visco Products Co., Inc., speak on corrosion control in oil and gas wells. J. Wade Watkins of the U. S. Department of Interior Bureau of Mines spoke on application of dissolved gas corrosion research to waterflood problems.

A special Ladies Night meeting has been planned for June 8 at the Tropical Cafeteria in Oklahoma City.

Alamo Section heard Maurice A. Riordan of Rio Engineering Co., Houston, speak on cathodic protection of well casings at the April 14 meeting.

A color film titled "City in the Sun" was shown at the March 17 dinner and program meeting.

East Texas Section officers for 1959 are Chairman W. R. Carroll, Humble Oil & Refining Co., Overton, Vice Chairman Omar L. Emrich, Tidewater Oil Co., Scroggins, Treasurer Gene E. Smith, Lone Star Steel Co., Gilmer, Secretary Ike H. Hartsell, Tretolite Co., Gladewater, and Trustee Jim Orchard, Nocor Chemical Co., Longview.

B. M. Davis of Davis-Kemp Machine & Tool Co., Kilgore, spoke on the use of plastic in casing repairs at the March 24 meeting.

Meetings dates for 1959 have been set for May 26, September 22, October 27, November 24 and December 15. These meetings will be held at the Longview Hotel in Longview.

Panhandle Section will hold its regular meeting May 26.

North Texas Section toured the production laboratory facilities of Sun Oil Co., Richardson, for its April 13 meeting program.

Shreveport Section for its April 7 meeting heard Dave Whiteman, Amoco Corp., Houston, speak on offshore corrosion control.

At the March 3 meeting, Maurice Belsom, section representative to the Science Education Council, was elected vice president of that council. He presented a survey of the council's activities. Program for the meeting was a paper presented by M. J. Olive, Arkansas Fuel Oil, on cathodic protection maintenance.

Teche Section will hold its May 21 meeting at the Petroleum Club in Lafayette, La.

Maurice A. Riordan of Rio Engineers, Houston, spoke on cathodic protection of oil and gas well casing at the March 26 meeting.

The third annual Corrosion Control Short Course sponsored by the section will be held June 2-4 on the campus of Southwestern Louisiana Institute at Lafayette.

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Best, Greco and Gribble Are Nominated for Offices

Maitland, Dorsey And Rench Named For Directorships

Nominations of candidates for election to the highest offices in the National Association of Corrosion Engineers have been received from the nominating committee. Officers elected will serve for the 1960-61 term. George E. Best is nominated for president; E. C. Greco for vice president and C. G. Gribble, Jr. for treasurer.

Nominated for terms on the board of directors were T. J. Maitland to represent NACE active members and J. E. Rench and J. S. Dorsey to represent corporate members.

Nominations made by the committee can be supplemented by nominations from active members of NACE in accordance with Paragraph Three of Section 3, Article VIII of the NACE Articles of Organization which states:

"Not later than a date to be fixed as provided in Section 5 of this Article, (Article VIII). The Secretary shall inform all members of the Association, by publication or otherwise, of the list of nominees reported to him by the Nominating Committee; and at any time prior to a later date, to be fixed as provided in Section 5 of this Article, additional nominations may be made by petition forwarded to the Secretary and signed by at least twenty-five (25) Active Members. Any such nominees for the office of President, Vice-President or Treasurer shall qualify as provided in the first paragraph of this section."

As indicated by the schedule published on this page, active members have until July 10 to submit the names of additional nominees by petition. Voting will be by letter ballot in August, with September 23 the deadline for votes to be in Central Office. Tellers will have until December 11 to prepare their report of the ballot count.

BIOGRAPHIES

GEORGE E. BEST, technical adviser to the general manager of technical service, Solvay Process Division of Allied Chemical Corporation, Syracuse, N. Y., was elected NACE vice president for 1959-60. His NACE activities include membership on the board of directors and the executive committee, chairmanship of the Baltimore Section and the Northeast Region, member of technical program committees, awards committee and symposia chairman. Several of his corrosion papers have been published in COR-ROSION. He has been in corrosion control work for 15 years.

E. C. GRECO, senior research chemist of the research department, United Gas Corporation, Shreveport, La., was appointed chairman of the NACE Technical Practices Committee for 1957-59. Previous NACE offices he has held include chairman of Technical Committee T-1, vice chairman of Technical Committee T-1K, vice chairman of Technical Practices Committee (1955-57), chairman of symposia at the 1954 South Central Region Conference and at the 1955 NACE Annual Conference. Three of his technical articles have been published in COR-ROSION. He is councilor of the American Chemical Society, has been president of the Louisiana Academy of Sciences and is a member of the American Association for the Advancement of Sciences.

Best   Dorsey

Greco   Gribble

Maitland   Rench

C. G. GRIBBLE, Jr., district manager for Metal Goods Corporation, Houston, Texas, is currently on the NACE board of directors as director representing corporate members. Active in the Houston Section, he has held most of the offices in that section including chairman in 1952. On the national level he has been chairman of the local arrangements committee for the 1952 Annual Conference in Galveston and co-chairman for exhibits at the 1957 Conference in St. Louis.

J. E. RENCH, manager of industrial paint sales for Napko Paint and Varnish Company, Houston, Texas, has been active in NACE technical committees on coatings and helped organize the first paint short course held in the Houston area. He also helped organize the Houston Coating Society and has participated in short courses sponsored by NACE.

J. S. DORSEY, corrosion engineer with Southern California Gas Company, Los Angeles, is active in NACE Technical Committees T-2B and T-7E and has been an officer in both committees. He served as an officer on the 1958 Western Region Conference committee and has been engaged in corrosion control work since 1944.

T. J. MAITLAND, electrolysis and protection engineer with the Long Line Department, American Telephone & Telegraph Company, New York City, is currently chairman of the Technical Practices Committee. He is also chairman of NACE Technical Committees T-2B, T-4B and T-4B-1. Several of his technical papers have been published and presented at national conferences. A former faculty member of the University of New Hampshire, he has devoted his career to corrosion control, cable construction and maintenance methods of long distance telephone cables.

Official Report of the NOMINATING COMMITTEE

The Nominating Committee at its March 20 meeting selected the following nominees for officers and directors for terms beginning March 18, 1960:

For President:

     George E. Best, Solvay Process Division, Allied Chemical Corp., Syracuse, N. Y.

For Vice President:

     E. C. Greco, United Gas Corp., Shreveport, Louisiana.

For Treasurer:

     C. G. Gribble, Jr., Metal Goods Corp., Houston, Texas.

For Director to represent active membership

     T. J. Maitland, American Telephone & Telegraph Company, New York City.

For Director to represent corporate membership:

     (two to be elected)

     J. S. Dorsey, Southern California Gas Company, Los Angeles, California.

     J. E. Rench, Napko Corp., Houston, Texas

Schedule of Dates For Nomination and Election of National Officers and Directors For Terms Beginning March 18, 1960

ACTIVITY	DATE TO BE COMPLETED
Formation of Nominating Committee (completed)	March 20, 1959
Nomination of Candidates and report to the Secretary (completed)	April 1, 1959
Publication of Nominating Committee report	May 1959 issue of CORROSION
30 to 35 days for members to prepare and file nominations by petition	June 10, 1959
Preparation and mailing of letter ballots to NACE members	July 21, 1959
Period allowed for members to return letter ballots	September 23, 1959
Period allowed to count ballots and prepare report by tellers	December 11, 1959
General Business Meeting	March 16, 1960

List of Members Eligible for Nomination to the Office of President, Vice President or Treasurer of the National Association of Corrosion Engineers for the Term Beginning March 18, 1960.

J. P. Barrett, N. E. Berry, G. E. Best,* H. L. Bilhartz, R. A. Brannon, E. G. Brink, H. R. Brough, J. Pat Casey, Jr., W. R. Cavanagh, Stephen P. Cobb, F. E. Costanzo, Stephen D. Day, Irwin C. Dietze, L. B. Donovan, M. G. Fontana, E. C. Greco, C. G. Gribble, H. F. Haase, Norman Hackerman, H. L. Hamilton, J. W. Harris, Tom L. Holcombe, Derk Holsteyn, A. N. Horne;

R. B. Hoxeng, L. A. Hugo, H. A. Humble, V. N. Jenkins, T. F. P. Kelly, V. V. Kendall, W. J. Kretschmer, R. E. Kuster, F. L. LaQue, C. P. Larrabee, R. J. Law, R. H. Lynch, E. D. McCauley, R. McFarland, Jr., George B. McComb, F. J. McElhatton, V. V. Malcom, T. P. May, R. B. Mears, E. F. Moorman, C. G. Munger, A. R. Murdison, W. R. Myers, E. P. Noppel, G. R. Olson;

Ivy M. Parker, R. R. Pierce, Robert Pope, E. C. Range, W. F. Rogers, L. F. Scherer, H. W. Schmidt, L. R. Sheppard, Edward L. Simons, A. D. Simpson, Jr., J. C. Spalding, Jr., D. E. Stearns, A. L. Stegner, E. H. Tandy, R. S. Treseder, H. M. Trueblood, H. C. Van Nouhuys, E. D. Verink, Jr., Aaron Wachter, H. E. Waldrip, T. R. B. Watson, L. C. Wasson, John B. West, F. L. Whitney and Guy F. Williams.

*Eligible for nomination for President only.

From the Desk of Your EXECUTIVE SECRETARY
T. J. Hull, Executive Secretary

• Active and Corporate Member Dues To Be Increased in 1960

The president of NACE announced at the General Business Meeting held at Chicago that the association's board of directors had approved increasing Active (individual) and Corporate (company) membership dues effective with dues payable in 1960. Active member dues are to be increased to $15. Corporate member dues will be increased to $150.

The last change in NACE dues structure was made in 1954 and effective with 1955 dues. This change increased Active member dues from $7.50 to $10. Corporate member dues have not been increased since this grade of membership was authorized.

A thorough study of the association's finances was made by the NACE Finance Committee in 1958. The study indicated that the association's margin of income over expenses during the past four years had been in the order of 2 to 3 percent. In the opinion of the Finance Committee and the NACE Board, this margin of income over expenses is not sound. In the opinion of the Finance Committee, Executive Committee and and board of directors, the association should have a margin of income over expenses that would amount to 8 to 10 percent of its annual income.

The association's expenses have increased from $266,264 in 1955 to $344,571 in 1958, while the association's income has increased from $277,121 in 1955 to $354,888 in 1958. Increased costs in all phases of the association's Central Office activities and in the publication of CORROSION account for the expense increase. The association membership since 1955 has increased from 5,107 to 6,297. Seven new sections have been formed and the services rendered by Central Office to regions and sections have increased and are being taken advantage of by many more regions and sections than in 1955.

• Visits to NACE Sections

The Board of Directors has authorized the executive secretary or his appointed representative from Central Office staff to visit with officers of as many sections as is possible during the next year. The purpose of these visits will be to determine what services and assistance is desired by sections and to acquaint section officers firsthand with existing services rendered by Central Office. The assistance of section officers also will be enlisted in obtaining information on prospective corporate members and where possible in the actual solicitation of new corporate members. Where possible, visits will be made to coincide with section meetings.

• Publications

CORROSION magazine showed a small net over expenses for 1958. Total revenue and expenses increased. The 124 technical papers published occupied 598 pages. The Publication Committee reported a large backlog of approved manuscripts on hand and requested a supplementary appropriation for the printing budget, which was granted.

The 1960 outlook is good, because of a scheduled increase in advertising rates, which is not expected to materially affect the number of advertising pages, principally because the rates presently being charged are considered to be lower than those of comparable technical journals.

Furthermore the Publication Committee is expected to ask for an increase in the allottment to the magazine from the increased dues effective in 1960.

Increased revenue is expected to be sufficient to permit expansion of both the Technical and Technical Topics sections, so the interval between receipt of a manuscript for review and its publication will approach three months.

• Coatings Papers Solicited

NACE members are asked to contribute and seek to encourage the contribution of worthwhile technical papers on coatings for publication in CORROSION. The number of technical papers on coatings has not kept pace with the general increase in technical material available.

• Abstract Card Service Survey

In October, 1958 the Publication Committee after approval by the executive committee instructed Central Office to make a survey of the NACE membership to determine the demand and potential use of an abstract search service. The survey was made in January, 1959. The results indicated that only a small number (less than ½ of 1 percent) could be expected to make use of a literature search service. So the Publication Committee at its meeting in Chicago agreed to drop the subject for the time being.

• Abstract Punch Cards

The subscription price to the NACE Abstract Card Service was increased from $100 to $175 beginning with the 1959 subscriptions. To date, 75 subscriptions have been received for the 1959 service. Nineteen subscribers did not renew for the 1959 service. The number not renewed is of the same order as has been experienced previously. It is expected eighteen to twenty new subscriptions will have been obtained by the end of 1959. Total income from 1958 Abstract Card Service subscriptions was $9400. The present number of subscribers, will produce a total income of $13,125. Total income from Abstract Card Service subscriptions if the expected 20 new subscriptions are received will be $16,625.

• Bibliographic Survey of Corrosion

The 1954-55 volume of the Bibliographic Survey of Corrosion was published in May, 1958. It had been expected that $5750 would be realized in 1958 from sale of the new volume, and from previously published volumes. Total income from the sale of Bibliographic Surveys of Corrosion during 1958 was $11,613.50.

Central Office attributes this large volume to the promotion given to the new Bibliographic Survey. Ads were carried in several issues of CORROSION. A paid ad was placed in another technical publication. Direct mail notices were mailed to all members and subscribers of NACE

and to approximately 10,000 scientists and engineers who are not members of the association. Through the first three months of 1959, income from sale of the Bibliographic Surveys of Corrosion amounted to $793.

In October of 1958, the Executive Committee on recommendation of the Publication Committee, approved publishing the Bibliographic Surveys of Corrosion on annually rather than biennially. Work currently is being done on the Bibliographic Survey of Corrosion for 1956. It is expected this volume will be published in July or August of this year. Publication on an annual basis should make the surveys more attractive and result in a wider distribution.

• Railroad Corrosion News Letter

The editor of the Railroad Corrosion News Letter has agreed to place the responsibility for the News Letter in the hands of the Central Office editorial staff. Central Office is expanding the mailing list for the News Letter by supplimenting it with names of members from several other engineering associations. Justification for the News Letter is two fold: It performs an educational service to industry already represented in the NACE membership and it is to attract new NACE members from the railroad industry.

• 1959 NACE Conference

Paid registrants at the 1959 Conference totalled 1312 (budget figure was 1300). Of the paid registrants, 1011 were NACE members, 241 were non-members and 60 were ladies. There were 254 free exhibitor registrations. There were 223 exhibitor booth attendants and 647 exhibitor guests. There also were 42 representatives of the technical press who were given free registrations.

Total registration was 2481 (budget figure was 2455).

• Preprints

Orders were taken for 4063 copies of preprints of papers presented at Chicago. Income from preprints sales amounted to $2725. A preliminary accounting indicates the cost of printing may be slightly more than the income from preprint sales.

A questionnaire has been mailed to all authors of papers presented at the 1959 Conference seeking their views on a satisfactory NACE preprint policy. A summary of replies to questionnaires will be presented to the Executive Committee to be considered in formulating a policy for preprints for the 1960 NACE Conference.

The major deterrent to furnishing copies of preprints at the Conference is the fact that authors do not submit manuscripts to Central Office early enough to permit Central Office to preprint. Mr. McFarland, Chairman of the 1959 Technical Program, placed considerable emphasis on 1959 authors' submitting manuscripts to Central Office by January 9. On that date 13 of the possible 88 manuscripts had been received at Houston. Through correspondence, telegrams and telephone calls it was possible to get only 55 of the 88 manuscripts by the middle of the week prior to the conference. Of the remaining 33, nine have since been received. From past experience, Central Office estimates at least half of the remaining 24 will never be submitted while the balance will come in over the next six months.

Nominating Committee—

Any Active Member in good standing is eligible for nomination as a director to represent the Active Membership of the Association and any Representative of a Corporate Member in good standing is eligible for nomination as Director to represent the Corporate Members of the Association, except the following who are not eligible for nomination as an elected director for the term beginning March 18, 1960—because of the time limitation in Section 5, Article IV of the Articles of Organization.

List of Members Not Eligible for Nomination as Director for Term Beginning March 18, 1960.

J. P. Barrett, G. E. Best, H. L. Bilhartz, R. A. Brannon, E. G. Brink, F. E. Costanzo, W. F. Fair, Jr., H. P. Godard, C. G. Gribble, H. F. Haase, H. L. Hamilton, R. E. Kuster, R. McFarland, Jr., E. F. Moorman, C. G. Munger, A. R. Murdison, R. R. Pierce, E. L. Simons, J. C. Spalding, Jr., A. L. Steger, W. H. Stewart, E. H. Tandy, R. S. Treseder, H. E. Waldrip, L. C. Wasson, T. R. B. Watson, J. B. West, L. L. Whiteneck, and Guy F. Williams.

Executive Secretary—

● 1960 Conference

The first meeting of the 1960 General Conference Committee was held in Dallas on April 8. Preliminary plans concerning housing, registration, meeting rooms and entertainment were made. The second meeting of the conference committee will be held in June and by the time the Executive Committee meets in September, it is expected complete plans for the 1960 Conference can be submitted for approval.

● 1961 Conference

Walter A. Szymanski, Hooker Chemical Company, Niagra Falls, New York, has been appointed General Conference Chairman for the 1961 NACE conference, which will be held in Buffalo, New York. Mr. Szymanski has played an important role in the affairs of the Niagra Frontier Section since its formation and has participated in the planning and organization of regional meetings and short courses.

● Corporate Member Luncheon

The Corporate Member Luncheon held at Chicago was attended by 142 Corporate member representatives and guests. A brochure describing the activities of NACE was prepared for distribution at the luncheon.

Main speaker at the luncheon was L. L. Whiteneck, then president of NACE. Mr. Whiteneck's talk was well received.

● NACE Regional Meetings in 1959

For the past several years the president of NACE has attempted to attend as many of the NACE Regional meetings as is possible. For Dr. Godard to attend all the NACE Regional meetings scheduled in 1959, he would need transportation with a speed matching that of a ballistic missile. The schedule calls for five meetings in four weeks beginning September 29.

Preliminary information indicates all regions are expanding programs this year. Central Office is now making plans for promotion and gearing activities to prepare the necessary programs and other printing that will be required. With all regional meetings coming taking place in four weeks, the work load on Central Office is high for the two months preceding them. An effort is being made to coordinate deadlines so conflicts can be held to a minimum.

● Region and Section Funds

At the Board of Directors meeting held in December, 1958, the NACE By-Laws were amended to require each Regional Division and each Section to submit a statement of total income and expenses to the Secretary of the Association. The amendment was made on advice of the Policy and Planning Committee, which in turn had been advised by the association's attorney that an accounting of Region and Section funds should be included in the Association's accounting to the Internal Revenue Department.

● NACE Region and Section Operating Manual

The NACE Section Operating Manual has been in the hands of section officers since June, 1958 and it has been learned that many sections are using it to good

advantage. Comments and suggestions for improving the Section Operating Manual are solicited and will be considered by the Policy and Planning Committee by the time of the 1960 Conference.

First draft of the NACE Region Operating Manual was presented to the Policy and Planning Committee at Chicago. Since then, copies have been mailed to regional directors and chairmen with a request that suggestions be submitted as soon as possible. After a reasonable time, suggestions for revising the manual will be considered and incorporated, if pertinent, and the Regional Operating Manual submitted to the board of directors for approval.

In the opinion of the Policy and Planning Committee, the Regional Operating Manual will be of considerable aid in the smooth functioning of regional business and conferences.

● Educational Films

Scripts for the first two parts of the three-part film on Soil Corrosion of Pipe Lines has been completed and approved by the NACE Executive Committee. The two parts completed are on fundamentals and protective coatings. They are now being produced by the Petroleum Extension Department of the University of Texas. The University of Texas production schedule calls for both films being completed by the end of 1959. NACE will make them available to regions and sections, to short courses and to individual companies.

Work has not begun on the third part, which will be on cathodic protection.

● NACE Cooperation with Other Organizations

A complete report of NACE's cooperation and joint activities with other organizations was included in the Technical Practices Committee report to the President. (A summary will be published in June CORROSION.) Since the report was prepared, NACE assistance has been concluded on a project involving the National Association of Fan Manufacturers by Group Committee T-6 on protective Coatings. Arno J. Liebman, NACE's representative reported that the specifications for surface preparation and coating fan blades has been completed by NAFM. In 1955, the NAFM requested that NACE assist in these specifications.

NAFM is well pleased with the technical advice rendered through Mr. Liebman. When specifications are published, they will carry an acknowledgment that technical assistance on sections pertaining to corrosion was given by the National Association of Corrosion Engineers.

Following the conference in Chicago, an invitation was received in Central Office asking NACE to participate in a general conference sponsored by the American Standards Association to consider the standardization of shop-fabricated vertical and horizontal metallic storage and processing tanks. Dr. H. P. Godard appointed Walter H. Burton, General Chemical Division, Allied Chemical Corporation, to represent NACE at the conference.

Representation on an American Standards Association's committee is by invitation. If NACE is invited to participate in the work, NACE policy requires approval by the association's board of directors.

15th Conference
REPORT

Summary of Principal Events

- Over 2400 crowd 1959 Corrosion Show to make it one of most successful

- More than 70 technical committee meetings are held, some with overflow attendance

- Noppel retires as Policy and Planning Committee chairman after a decade of service

- Whiteneck cites NACE's value to industry at corporate member representatives' luncheon

- Announcement made of increase in active member and corporate member dues

- Added funds made available for earlier publication of paper in CORROSION

- Association makes small net gain in active and corporate members for 1958.

Full Schedule Occupies 2400 At Meeting

A full schedule of technical events occupied the 1600 registrants attending the March 16-20 Fifteenth Annual Conference and 1959 Corrosion Show at Chicago's Hotel Sherman. Total attendance was 2481. The serious business of corrosion control was leavened by appropriate social events and attention to administrative functions of the association.

The consensus of those taking part was that the 1959 program was another in the succession of fine NACE meetings, each one of which seems to be better than the last. Good reports about the meeting were especially evident among the 96 exhibitors, whose booths attracted sustained attention during the 3-day Corrosion Show.

Many of the 70-odd technical committee meetings were held in rooms overflowing with interested participants, while attendance at symposia held a high level throughout. Several hundred attended the Friday morning round table sessions.

Registration Smooth

Registration opened on Sunday afternoon and with the exception of a brief period of congestion Monday morning ran smoothly through the week with only nominal delays.

Handling of local arrangements and the multitude of details involved in the physical schedule for the program was done by a Chicago Section committee headed by D. B. Sheldahl, Sinclair Research Labs., Harvey, Ill. and Richard Rue, Insulmastic Corp., Summit, Ill.

In addition to the events of technical significance, the usual schedule of meetings of the association's board of di-

R. B. JANOTA, Swift & Co., Chicago, general conference chairman, confers with some of his co-workers during a busy week. Lower, left, E. P. Noppel, Ebasco Services, Inc., retiring chairman of the policy and planning committee is thanked for his years of service to NACE by President Whiteneck at the annual banquet.

TYPICAL SCENE at 1959 Corrosion Show where more than 2400 persons viewed the displays of 96 exhibitors on the mezzanine floor of the Sherman Hotel. Many exhibitors called the 1959 Show the best NACE has held in years.

1959 Corrosion Show Is Considered Very Successful

Ninety-six exhibiting companies comfortably filled the mezzanine floor exhibit area of the Sherman Hotel during the NACE Conference there in March. Proximity of the exhibit area to the principal technical and social functions of the meeting aided materially in the sustained traffic reported by most exhibitors. Many exhibitors rated the 1959 Corrosion Show very successful.

The Tuesday "free afternoon" had its expected effect in bringing onto the exhibit floor a substantial proportion of registrants. However, there was a steady flow of traffic during the whole three days of the show.

The final list of exhibitors is as follows:

Agra Engineering Co., Austin Screw Products Co., Plastics & Coal Chemical Division, Allied Chemical Corp.; Alloy Steel Products Co., Aluminum Company of America, Amercoat Corporation, American Hot Dip Galvanizers Association, Inc., American Smelting & Refining Co., Apex melting Co., Armour Chemical Division, Bishopric Products Co., Wayne Broyles Engineering Co., Burndy Corporation, A. M. Byers Co., Calag Chemical Co., Carboline Company, Carlon Products Corporation;

The Carpenter Steel Co., Cathodic Protection Service, Centriline Corporation, Charleston Rubber Company, Chicago Bridge & Iron Company, Chicago Metallizing Corp., Coast Paint & Lacquer Co., Cooper Alloy Corp., Corite Products, Inc., Corning Glass Works, Cosasco Division, Perfect Circle Corp., Crane Company, Dearborn Chemical Company, The DeVilbiss Company, The Dow Chemical Co.: Magnesium Anode Division, Saran Lined Pipe Division; The Duriron Company, Inc.;

Enjay Company, Inc., Erico Products Co., The Fibercast Co., The Garlock Packing Company, General American Transportation Corp., The Glidden Co., Good-All Electric Manufacturing Co., Gulf States Asphalt Co., Hanson Equipment Co., Harco Corp., Heil Process Equipment Corp., Hercules Powder Co., Hills-McCanna Co., The International Nickel Co., Johns-Manville Sales Corp., Polyken Sales Division, The Kendall Co., Kerr Chemicals, Inc., Koppers Company, Inc., Kraloy Plastic Pipe Company, Inc., Magnaflux Corp., F. H. Maloney Co., Metallizing Engineering Co., Inc., Midwestern Pipe Line Products Co., M. C. Miller Company and Minnesota Mining & Manufacturing Company;

National Carbon Company, Nicolet Industries Inc., Orchard Paper Co., Oregon Metallurgical Corp., Perrault Equipment Co., The Pfaudler Co., Chas. Pfizer & Co., Inc., Phelps Dodge Copper Products Corp., The Phillip Carey Manufacturing Co., Pittsburgh Coke & Chemical Corp., Pittsburgh Corning Corporation, Plicoflex, Inc., Radio Receptor Co., Inc., H. B. Reed & Co., Inc., Reilly Tar & Chemical Corp., Republic Steel Corp., Resistoflex Corporation, Royston Laboratories, Inc., Shell Chemical Corp.;

Shell Oil Company, Socony Paint Products Co., Solvay Process Division, Allied Chemical Corp., Standard Magnesium Corp., Steelcote Manufacturing Co., The Tapecoat Co., Texsteam Corp., Tinker & Rasor, Tretolite Co., Division Petrolite Corp.; Truscon Laboratories, Tube Turns Plastics, Inc., The U. S. Stoneware Co., Valdura Division, American-Marietta Co.; Victaulic Company of America, Visco Products Co., T. D. Williamson, Inc., Wright Chemical Company.

Salt water corrosion test results

Samples prior to testing	After 3 months' exposure	After cleaning & measuring
A-53 Steel	Heavy uneven coating of red rust underlaid with black magnetic oxide.	Areas of attack are localized. Max. pit depth 34 mils.
Low Alloy Cu-Ni Steel	Much the same as A-53 Steel. Heavy tuberculation produces small protuberances.	Surface is uneven, pitted, wavy. Max. pit depth 25 mils.
4-D Wrought Iron	Light coating is characteristic. No evidence of tuberculation.	Surface is uniform. No evidence of pitting.
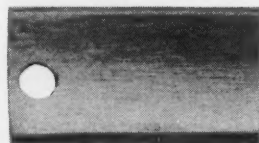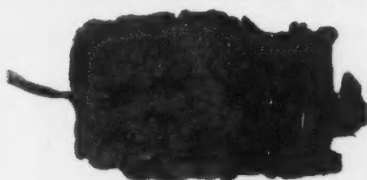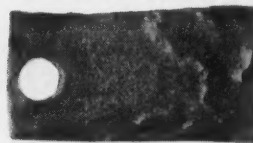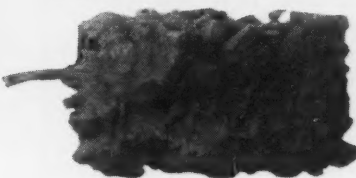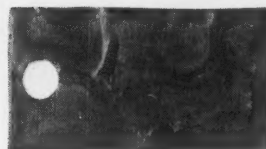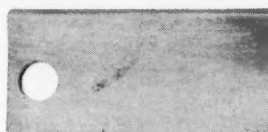
4-D Wrought Iron exhibits decided superiority in corrosion-resistance over other metals in three months' exposure tests in 3% aerated salt solution.

Recent testing at A. M. Byers Company Laboratories shows 4-D Wrought Iron wholly resistant to corrosive penetration while ferrous substitutes evidence severe pitting. Maximum depth of attack—in just three months—is 34 mils for A-53 steel and 25 mils for low alloy, copper-nickel steel.

This aerated salt water test is continuing and will be extended to one year. Further results will be published. We would welcome an opportunity to relate the results of this test—and other comparative corrosion tests—to your corrosion problems. Ask the Byers representative to call. Or write: Engineering Service Department, A. M. Byers Company, Clark Building, Pittsburgh 22, Pa.

Note: Comparable surface preparation was assured by checking with "Surfindicator."

TEST CONDITIONS

Test Medium—3% sodium chloride solution

Test Temperature—
Room temp.—68-75°F., average 70°F.

pH—Average 7.8

Aeration Rate—3400 cc./min. ±10%

Solution Volume—
32 liters replenished 3 times a week

Coupon Size—1″ x 2″ x ⅛″ to ¼″

Coupon Preparation—
Polished with 100-grit carborundum on a belt grinder

Test Period—3 months; data obtained monthly

Materials Tested—
4-D Wrought Iron—edges coated
A-53 Steel
Low Alloy Cu-Ni Steel

BYERS 4-D WROUGHT IRON

TUBULAR AND FLAT ROLLED PRODUCTS

ALSO AMBALLOY ELECTRIC FURNACE STEELS, PVC PIPE, SHEET AND ROD STOCK

Corrosion costs you more than Wrought Iron

NACE's Value to Industry Cited by Whiteneck

Corporate Member Luncheon Hears President Whiteneck

"This NACE pool of knowledge and experience accounts for 75 percent of the requirements for success (in controlling corrosion) and the 25 percent luck is up to you," President L. L. Whitneck told a meeting of corporate member representatives during the Chicago conference. He spoke to a luncheon gathering of 150 NACE corporate member representatives and guests on the value of NACE to industry in controlling corrosion.

In the quoted comment he was enlarging on the statement by former NACE president Mars Fontana of Ohio State University that solving corrosion problems is the result of 25 percent knowledge, 50 percent experience and 25 percent luck. Mr. Whitneck was emphasizing the important role of NACE in providing industry with a convenient vehicle for the collection and dissemination of corrosion knowledge and experience for the benefit of all industry.

The rapid growth of NACE is an indication of the necessity for the exchange of corrosion control information and its importance to industry and government, he said. Mr. Whitneck also cited some of the ways in which corporate members benefit both directly and indirectly from NACE's activity and from participation in its work by their engineers.

Mr. Whitneck also pointed out that the experience of the more than 6000 NACE members is made freely available to everyone and that the benefits from this policy far outweigh the monetary contributions to NACE by the companies benefiting.

BOOSTERS for the South Central Region Conference at Denver October 12-15 were these two Colorado members dressed in Western styles symbolic of Colorado's history. They are, left, Harold D. Doll, Corrogard, Inc., Boulder and, right, Edward L. Kent, Jr., Kohler-McLister Paint Co., Denver.

'60 Corrosion Show Brochures Are Mailed

Descriptive brochure and contracts for the 1960 Corrosion Show to be held at Dallas Memorial Auditorium, March 15-17 were mailed to prospective exhibitors during April. Persons or firms interested in this show may get copies of the information on request from R. H. Huff, Jr., NACE Exhibition Manager, 1061 M & M Bldg., Houston 2, Texas.

The show, to be held concurrently with the NACE 16th Annual Conference, will be the first in the Southwest since the 1952 NACE meeting at Galveston. A floor plan calling for about 120 booths has been prepared. This plan, together with information about the advantages of exhibiting in the Southwest, some statistical data on NACE shows and the necessary data on prices and contract terms is available now for distribtuion.

Because of the limted space available, Mr. Huff believes the 1960 show is likely to be sold out before the opening of the 16th Conference.

Baker and Adolphus to Be Headquarters at Dallas

The Adolphus and Baker Hotels have been selected as joint headquarters for the 1960 Sixteenth Annual Conference to be held in Dallas March 14-18. The 1960 Corrosion Show will be held concurrently March 15-17 at Dallas' new Memorial Auditorium.

Meetings scheduled for Monday March 14 will be held at the Adolphus hotel and those scheduled for March 15-18 at the auditorium.

The general conference committee held its first meeting April 8 at Dallas to make initial plans.

Active Member Dues Are Raised To $15 Annually

Dues for active membership in the National Association of Corrosion Engineers will be $15 annually effective with the 1960 calendar year. President L. L. Whiteneck, addressing the annual membership meeting of the association at the Sherman Hotel in Chicago also announced that dues of corporate members will be increased to $150 a year beginning in 1960.

President Whiteneck gave a brief account of the association's activities during 1958 and pointed to the following activities, among others, as being significant:

1. A sustained effort to attract new active and corporate members is being made by NACE Central Office.
2. The association is cooperating in the presentation of nine corrosion control short courses during 1959.
3. A study is underway to determine the feasibility of constructing a building to house Central Office activities at Houston.
4. The practice of requiring persons seeking to renew lapsed membership to pay double dues when they have failed to formally resign from the association has been discontinued. Henceforth members renewing lapsed memberships will be required to pay dues only for the current year.

Full Schedule—

rectors and of various standing committees was carried out. The general business meeting, at which the association's officers and chairmen of standing committees make their reports was well attended.

The annual banquet had its complement of events, including the presentation to Dr. Aaron Wachter, Shell Development Co., Emeryville, Cal. of the 1958 Frank Newman Speller Award and of the 1958 Young Author Award to D. W. Juenker for his paper "Cavity Formation in Iron Oxide," published in the January, 1958 issue of CORROSION.

Noppel's Service Marked

The long service to the association of E. P. Noppel, Ebasco Services Inc., New York as a director and chairman of the policy and planning committee over the last decade was recognized when President L. L. Whiteneck presented him with a certificate of thanks from the association during the banquet.

As usual incoming directors and other officials concerned with present and coming events sponsored by the association were introduced.

The association also was honored again by the presence of Frank N. Speller, after whom the Speller award is named. Dr. Speller is still an active corrosion consultant. •

Over 40 foreign countries are represented by CORROSION subscribers.

Many Sessions of Technical Committees Are Held With "Standing Room Only" at Chicago

"Standing room only" attendance at many of the meetings of NACE technical committees during the March 16-20 Fifteenth Annual Conference in Chicago further underlined the importance of committee work in corrosion control progress. Capacity attendance is becoming increasingly common both at national and at regional sessions at which technical committees meet.

Reports from the meetings often indicate sessions are devoted to informal discussion of corrosion problems. This approach is viewed by many as being equally fruitful in extending information to that obtained in formal symposium-type presentations. The free exchange of experiences among workers in like fields further underlines the importance of personal attendance at committee sessions.

Some Formal Programs

Other sessions featured presentation of formal programs. In the case of surface preparation, for example, the availability of graphical representations that can be used as standards of reference is particularly useful. The committees dealing with water corrosion problems displayed examples of the effects of potable water on piping systems.

A majority of those registering for the conference attended one or more committee sessions during the 5-day meeting. Minutes of proceedings at ses-

INTENSE CONCENTRATION on corrosion problems in their respective spheres of interest is shown in these views of presiding officers at technical committee meetings. Top, left, F. H. Meyer, National Lead Co. of Ohio, Cincinnati, vice-chairman of T-5A-5 on Nitric Acid and right, C. P. Dillon, Union Carbide Chemicals Co., Charleston, W. Va., chairman of T-5A on Corrosion in Chemical Processes are shown. Bottom, W. T. Burges, Metropolitan Utilities District, Omaha, chairman of T-4F on Material Section for Corrosion Mitigation in the Utility Industry presides at his committee's meeting. Below, right, L. F. Heverly, Trans-Canada Pipelines, Inc., Toronto presides at a session of T-2D on Standardization of Procedures for Measuring Pipe Coating Leakage Conductance.

Three Interim Reports Are Heard by T-6D-2

Three interim reports were made and a report of T-6D-2 on Standardization of Scope of Painting Specifications was made ready for presentation to T-6 for approval at a meeting of T-6D in Chicago. T-6D on Industrial Maintenance Painting has R. H. Bacon, Dow Chemical Co., Freeport as chairman. He presided over the meeting attended by 53.

The committee decided also to appoint two new task groups on Painter Safety and on Painter Education. Exploratory Task Group T-6D-5 was terminated after this recommendation.

Joint Report on Stress Corrosion Nearing Completion

The joint American Society for Testing Materials-National Association of Corrosion Engineers task force report on stress corrosion cracking is finished except for two sections, both of which are now near completion, members of T-5E on Stress Corrosion Cracking of Austenitic Stainless Steel learned at a meeting in Chicago March 19. Plans have been made tentatively to have the report published by ASTM which will make copies available to NACE at a discount.

Members agreed the report should be published as quickly as possible. It also was considered desirable that the NACE committee continue to function, perhaps as a means of accumulating experience data from industry.

Spontaneous discussion concerning industry practice as to types of coupons used in stress corrosion cracking tests developed useful information. The following types of coupons were discussed:

1. Sheared edges and stencil marks.
2. Erickson cup-type made in a ½-inch ball bearing and mating die to deform material approximately ⅛-inch thick.
3. 3-inch square, ⅛-inch or less thick with one sheared edge and others saw cut. Also welded under restraint.
4. Circular weld on 3-inch square plate.
5. One-inch square block severely abraded all sides.
6. One-inch tubular sections flattened.
7. Horseshoe-type samples.
8. Stressed tension-type samples.
9. Thermally stressed samples.

The subject of types of test coupons was put on the agenda for discussion at future meetings.

Some of the other subjects covered were effect of tin on copperbase alloys in steam or ammonia environments, to what extent is stress-relieving beneficial?, performance of two-phase alloys compared to single phase austenitic steels, susceptibility to stress corrosion cracking of cast vs wrought stainless steels.

Many Sessions—

sions will be prepared in many instances and forwarded to members unable to be present.

How to Join Committees

Many NACE members do not know the procedure for joining a technical committee. The interested member may apply directly to the chairman of the committee in which he is interested or write to F. Vander Henst, Technical Committee Secretary, NACE, 1061 M & M Bldg., Houston 2, Texas, indicating his field of interest. Mr. Vander Henst will forward his letter to the appropriate committee chairman so he can be enrolled.

Members enjoy the advantage of receiving copies of minutes and of having the opportunity to contribute toward the committee's work in numerous ways.

AMONG 70-ODD technical committee meetings were, top, T-2K Prefabricated Film for Pipe Line Coating is presided over by H. D. Segool, Kendall Co., Chicago, vice-chairman; middle, T-2H Asphalt Type Pipe Coatings committee hears Frank B. Burns, General Asphalt Inc., Wynnewood, Okla. chairman and bottom, Task Group T-6A-17 on Polyeurethanes is presided over by Richard Sansone, Mobay Chemical Co., Pittsburgh, chairman.

Savings on Surface Preparation Costs Reported to T-6G

Substantial savings in cost of preparing the surfaces of steel using venturi-type blasting nozzles was reported at a meeting of T-6G on Surface Preparation for Organic Coatings at Chicago. Eighty members and visitors attended the meeting at which J. Bigos, United States Steel Corp., Monroeville, Pa., presided. The committee also heard a discussion of Swedish and American Society for Testing Materials surface preparation standards, an account of research under way by the Steel Structures Painting Council and an extensive discussion on sandblasting techniques and economics.

The committee was told also that the Civil Works Division, Corps of Engineers will continue its surface preparation studies and report on them at the committee's meeting next year.

J. Bigos was nominated to be permanent chairman and John Keane, Steel Structures Painting Council as vice-chairman.

Weld Cleaning Methods

Steel Structures Painting Council work currently is directed toward cleaning and treating welds. Excellent results have been obtained from very simple treatments, including a water wash. Studies of the effect of rust on paint life are continuing and several new projects have been started, including the use of paint additives to improve surface wetting characteristics, the use of weathering to remove mill scale and others.

A report on actual tests designed to produce examples of "white metal, commercial and brush-off" sandblasting was given by Ed Oakes, Clementina, Ltd., Houston, Texas. Because the end condition varies with the initial condition of the surface, Mr. Oakes indicated it is necessary for those concerned to set up

a blast cleaning procedure whenever there is any doubt about the suitability of specified sandblast standard.

Local sands can be just as good as commercial sands hauled long distances and reduction in costs through use of the proper local sands can be substantial. Tests using a modified version of the SSPC venturi nozzle showed it to be effective. Cost comparisons showed that brushoff blast cleaning ran 2½ cents a sq. ft.; commercial 7 cents and white metal ranged from 13 to 45 cents, depending on the initial condition of the surface.

Using local sand and the venturi nozzle comparable costs were: Brushoff, 1¾ cents a sq. ft.; commercial 5 cents and white metal from 9 to 19 cents.

Less Sand Used

John Rohwedden, Corps of Engineers, Rock Island, Ill., reporting on large scale tests under way, said it had been learned that best results were obtained using less sand than usually quoted as recommended amounts. Little effect was noted from changed nozzle lengths after reaching 5 to 6 inches and there is little effect from angle.

Tank Car Exterior Coatings Are Discussed

Twenty persons participated in a discussion of exterior coatings for railroad tank cars during a meeting of T-3E-1 on Corrosion of Railroad Tank Cars at Chicago. J. R. Spraul, General American Transportation Corp., Chicago, chairman presided. The group also considered the removal of interior coatings and linings and problems associated with tank car fittings.

Tanker Problems Covered

Forty-eight persons participated in a 2½ hour discussion of tanker corrosion problems during the Chicago meeting of T-3H on Tanker Corrosion. W. S. Quimby, The Texas Co., Beacon, N. Y., presided.

Report on Acidproof Brick Floors Discussed

A draft of the report on "Acidproof Floor Construction with Membrane and Brick," was reviewed at a meeting of T-6K on Corrosion Resistant Construction with Masonry and Allied Materials at Chicago during the 15th Annual NACE Conference. L. R. Honnaker, E. I. duPont de Nemours & Co., Inc., Wilmington, Del., chairman, presided over the meeting attended by 23.

Suggested as possible subjects for future committee activity were prestressed linings for vessels, masonry lined pressure vessels, acid resisting stack construction and chemical-resistant concrete.

SPECIMENS OF CORRODED water pipe were shown during the meeting of T-4E on Corrosion by Domestic Waters. The committee is headed by T. E. Larson, Illinois State Water Survey, Urbana.

Chlorine Mixtures Survey Summary Is Discussed

"A Summary of Replies to a Questionnaire on Handling Various Chlorine Mixtures" was discussed, corrected and submitted for approval by T-5A-4 on Chlorine during a meeting in Chicago. L. W. Gleekman, Wyandotte Chemicals Corp., Wyandotte, Mich., chairman presided over the sessions attended by 21.

T-6E Session Is Held

H. E. Waldrip, Gulf Oil Corp., Houston presided over a meeting of 20 members and guests of T-6E on Protective Coatings in Petroleum Production at Chicago. The discussion covered metallic silicates, galvanizing metalizing, holiday detectors, inspection, choosing a contractor and well tubing.

Rock Shield Specifications

Specifications for rock shield are expected to be completed soon by Task Group T-2J-5, it was announced at a meeting of T-2J on Wrappers for Underground Pipe Line Coating at Chicago. R. A. Brannon, Humble Pipe Line Co., Houston chairman presided at the meeting attended by 31.

More Money Allocated To Corrosion Printing

The NACE board of directors has authorized the expenditure of additional sums, up to $10,000 during the remainder of this calendar year for the publication of technical papers in CORROSION. The board took this action on recommendation from the Publication Committee, which aims to reduce the time interval between submission of a paper and its publication in CORROSION.

The Publication Committee also discussed other aspects of the association's business involving publications, notably, the functions of the editorial review and abstract subcommittees, the proposed corrosion abstract search service, a 10-year index to the bibliographic surveys of corrosion, a 5-year index to CORROSION and other matters.

T. P. May, The International Nickel Co., Inc., Harbor Island, N. C. presided over the sessions as interim chairman during the absence abroad of R. S. Treseder, Shell Development Co., Emeryville, Cal., chairman.

Association's Fiscal Operations in 1958 Show Only Small Net Over Expenses

Report by
A. L. STEGNER, Treasurer

Consistent with past operations, the NACE fiscal year ended with a small difference between income and expense.

Income for the year 1958 from regular business exceeded the budget only slightly.

Income from publications and the 1958 Conference was slightly less than budget.

Regular business and publication expenses were lower than the budget amount but expenses for the 1958 Conference were higher.

Figures show income and expenses for 1958.

Figure 1 represents the NACE membership growth. The bottom curve, representing Junior members, shows an increase of one, with a total of 31. The next curve shows an increase in corporate members of four, with a total of 390. Actually, 34 new corporate members were gained during 1958 but 30 of the existing corporate members were dropped during the year.

There was an increase of 260 active members to a total of 5,264. Actually, 574 active members joined during 1958 but 314 active members were dropped on December 31 for non-payment of 1958 dues. The top curve represents total members, which was 6,085 on December 31. This figure has increased somewhat since then.

Figure 2 shows income for the year 1958 compared to previous years. The bottom line represents conference income, which was $61,145 in 1958. The next curve represents income from regular business, which was $92,474 in 1958. The next curve represents income from publications, which was $201,270 for the year 1958, and the top curve represents total income, which was $354,889 for the year 1958.

Figure 3 shows expenses for the year. The area between the total income curve and total expense curve represents the association's equity. The bottom curve represents conference expense, which was $37,545 for 1958. The next curve represents regular business expense, which was $107,004 for the year 1958. The next curve represents publication expense, which was $200,023 for the year 1958. The next curve represents the total association expense, which was $344,572 for the year 1958. The top curve represents total income, which was $354,889 in 1958.

The difference between total expense and total income curves for the year 1958 represents the 1958 addition to equity, which was $10,317. Total associa-

TYPICAL SCENE showing A. K. Long, Glidden Co., Cleveland, answering questions from the floor following presentation of his paper, "An Approach to Protective Coating Engineering," during Part 2 of the Protective Coatings Symposium. Discussion records were received on 60 of the papers given at Chicago, the largest number in recent years. Standing at Mr. Long's left is H. W. Foelsch, Lithcote Corp., Melrose Park, Ill., symposium chairman.

tion equity as of December 31, 1958, was $205,325.

A condensed balance sheet for the association's finances on December 31, 1958 is given below.

Looking at Figure 3 again, we see that the association's margin of income over expenses for the year 1958
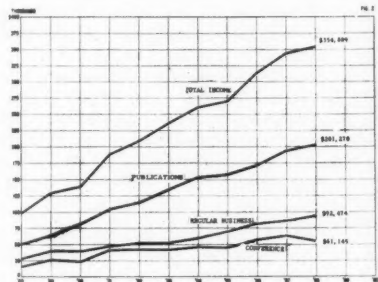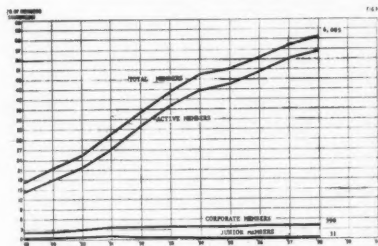
Condensed Balance Sheet at Dec. 31, 1958

Assets		Liabilities & Association Equity	
CURRENT ASSETS		**CURRENT LIABILITIES**	
Total	$157,308	Total	$ 1,706
INVESTMENTS		**AMTS. REC'D IN ADVANCE**	
Shares in Savings Assns.	133,000	Total	83,876
SPECIAL FUNDS		**REVENUE DEFERRED**	
Educational Funds	1,573	Total	21,365
FIXED ASSETS—AT COST		Contributions For Research and	
Office Furn. and Equip.	24,288	Educational Purposes	
Less: Reserve for Depr.	12,649	Total	1,524
Fixed Assets—Net	11,639		
DEFERRED EXPENSES	10,276	**ASSOCIATION EQUITY**	205,325
		TOTAL LIABILITIES	
TOTAL ASSETS	$313,796	**& EQUITY**	$313,796

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"industry looks to NACE for Leadership and Action"

Comments by Aaron Wachter after receiving the NACE 1958 Frank Newman Speller Award at Chicago during the 15th Annual Conference, March 16-20, 1959.

TO YOU, Bill Stewart and the members of the Award Committee, to the board of directors and to the association I wish to express deep appreciation of the great honor that this award represents to me and to my associates. Our work in the field of corrosion prevention has been a team effort with a remarkable spirit of cooperation. In particular among my collaborators at Shell Development Company I should mention the names of R. S. Treseder, P. J. Raifsnider, R. F. Miller, M. K. Weber, Rita Wieland and E. W. Haycock.

I have been in the field of corrosion for 20 years now and have witnessed the truly remarkable growth of this field. Great strides have been made in its technology, supported and stimulated by recognition of its importance in industry, in defense and in academic circles. The question might arise—Where do we go from here? What of the future? Can we extrapolate from past experience? In part we can, but I do not believe we can get an accurate conception judging only from the past. The picture would be much too conservative.

Aaron Wachter, since 1938 head of the corrosion department of Shell Development Co., Emeryville, Cal. Dr. Wachter, NACE president in 1954, has been active in NACE in numerous executive and technical capacities. He is author and co-author of numerous technical papers on corrosion control published by NACE and elsewhere.

There is no question that we are in an age of rapidly accelerating technological advance involving all industries. Also, new industries spring into existence and become huge almost overnight. All these activities give rise to greater demands on corrosion engineering. The chemical, petroleum and other process industries are turning for future growth to processes with violently reactive reagents at higher temperatures and pressures. Communications, transportation, electronic and computing machine industries (to mention only a few) will be increasingly concerned with reliable performance of their complex and closely engineered units under all conditions. New activities and further expansion in nuclear power and in rocketry give rise to demands on corrosion technology which are of critical importance. In fact, to an increasing degree in all industries, new advances are found to depend on ability to overcome critical corrosion difficulties.

There is another aspect that should be recognized. We are living in a country with an increasing standard of living for everyone. This means that costs for maintenance, repair and replacement of equipment are high and will go higher. Industry will find (some already have) that they simply cannot afford to tolerate

such charges and will have to have accurate, reliable, preventive corrosion engineering.

It is popular these days to compare American activities in various fields with those in Russia. I don't have extensive data for such comparison, but it is interesting to learn that last year the USSR held a conference on corrosion in Moscow attended by several thousands of their scientists and engineers at which some 200 papers were presented. I am also informed that **all** engineering students are required to complete a one-semester course in corrosion at the University of Moscow. It would seem that they are determined not to let their side of the iron curtain get rusty! These slight indications are worth serious thought and should at least keep us from feeling too complacent about our progress.

In looking ahead I see varied, challenging opportunities and increasing need for corrosion engineers. The field is alive and growing. To a large degree the future of corrosion engineering depends on this association. Industry and the Nation look to the NACE for leadership and action in meeting and anticipating growth requirements for the profession. The responsibility is here, it is yours. I have every confidence in the outcome. The future looks good!

"in all industry new advances are found to depend on ability to overcome critical corrosion difficulties."

Association's Fiscal—

amounted to only 2.9 percent of the total association income for the year.

You will also notice from the total income and total expense curves that this margin has varied from 6 to 2.9% over the past four years.

At this point, I would like to say that the publisher that prints CORROSION magazine gave the association a credit of over $5,000 at the end of the year, reflecting the efficiency with which the CORROSION staff worked with the publishing company during the year. Without this credit, the association's margin of income over expenses for the year would have been approximately $5000 or only 1.8 percent of the total income.

Your Finance Committee had a meeting to discuss the association's budget for 1959, reviewed in detail the association's income and expenses since 1955. 1955 was selected because that was the year in which the association realized an increased income from the increase in active member dues.

In the treasurer's report of the Finance Committee's meeting, he reported that the committee, after reviewing the association's net income over expenses for the past several years and the proposed budget for 1959, was urgently concerned about the very small association operating margin. This has been in the order of 3% to 4% since 1955 and without the publication refund from the printers of the magazine would have been only 1.8 percent.

The Finance Committee was of the
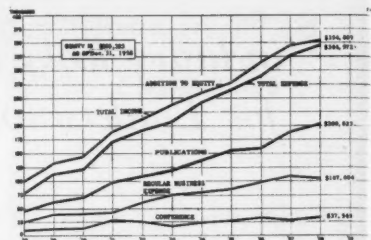
firm opinion that an operating margin of this small a percentage is an unsound financial practice. The committe, therefore, recommended to the board of directors that the association's annual income be increased through increased active and corporate member dues and items of income from publications. The Finance Committee also recommended that the increase in income should be large enough that Regular Business and Publications would be self-sustaining and that the annual association net income over expenses would amount to from 8 to 10 percent of the annual income.

1961 Conference Chairman

Walter A. Szymanski of Hooker Chemical Company, Niagara Falls, N. Y., has been appointed General Conference Chairman for the 1961 NACE Annual Conference to be held in Buffalo, N. Y. He has been active in the Niagara Frontier Section since its formation and has helped plan and organize regional meetings and short courses.

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GENERAL NEWS

University of Missouri Sets June 8-12 Maintenance Coatings Short Course

A 5-day short course on maintenance coatings will be held June 8-12 at the University of Missouri School of Mines and Metallurgy, Rolla. Wouter Bosch, professor of paint and polymer chemistry at the school, is director of the course.

The program is as follows:

Monday, June 8

Relation of Building Blocks to Properties and Performance of Coatings by Wouter Bosch.

Tuesday, June 9

Proper Selection, Use and Performance of Maintenance Coatings, R. E. Gwyther, The Sherwin Williams Co., Cleveland.

Hotel Maintenance, William Lorenz, Chief Engineer, Hotel Cornhusker, Lincoln, Neb.

Wednesday, June 10

Theories and Types of Corrosion by Walter T. Schrenck, professor of chemical engineering, School of Mines and Metallurgy.

Prepare and Paint—or Repair, J. C. Leslie, Tnemec Co., Inc, North Kansas City, Mo.

Thursday, June 11

Institutional Maintenance Painting, Ray N. Elvart, Ray N. Elvart & Co., Chicago.

Organization of a Painting Program, Charles W. Sisler, Monsanto Chemical Co., St. Louis.

Painting Cost Control by the Numbers: Statistics Can Point Out the Weak Spots in Your Procedures, Charles W. Sisler.

Friday, June 12

Rollers for Every Painting Purpose, John L. Touchett, EZ Paintr Corp., Milwaukee.

Exposure Sites Requested For Welding Council Tests

A search for industrial exposure sites is being conducted by the High Alloys Committee of the Welding Research Council. The sites are to be used to determine what industrial process media cause intergranular attack of austenitic stainless steels.

Descriptions of possible sites should be sent to R. M. Fuller, International Nickel Company, Inc., 67 Wall Street, New York 5, N. Y.

Several hundred corrosion test racks containing welded and unwelded specimens with a variety of heat treatments have been prepared.

The tests will also be used to evaluate the boiling 65 percent nitric acid test as a method for predicting intergranular corrosion susceptibility.

Spraying Unlimited, Irvin B. Thomas, The DeVilbiss Co., Toledo, Ohio.

Dormitory housing is available for single and married persons. Registration fee is $25, payable to Dr. Wouter Bosch.

Also scheduled at Rolla are the following: July 6-17, Paint Short Course for Beginners, consisting of 20 lectures, 10 discussion periods and 10 laboratory sessions. There are no prerequisites.

On July 20-31 an Advanced Paint and Polymer Refresher Course will be held. Prerequisites are either a year of experience, BS in chemistry or chemical engineering or completion of the beginner's course.

Additional information on any of the courses and registration blanks are available on application to Dr. Bosch.

India Is Considering Corrosion Society Similar to NACE

An Indian organization similar to the National Association of Corrosion Engineers is being considered by scientists and engineers concerned with corrosion control work in India.

The first scientific symposium on corrosion and its prevention was held last December in Calcutta. It was organized by the Society for Corrosion and Coating Technology.

India's estimated annual loss to corrosion is 106 million dollars, according to J. N. Mukherjee, former director of the Indian Agricultural Research Institute and Central Building Institute. He gave the inaugural address at the Calcutta symposium.

A philosophical definition of corrosion was given in one of the symposium addresses: "Corrosion is a running down of matter along the incline of free energy, something like the unwinding spring, and all activity of the corrosion scientists is aimed to retard this fall along the free energy incline of matter. Our activity is merely an application of brake to the chemical process of ageing of matter as it were to act as wet blankets on the fiery enthusiasm of nature to devour the stored free energy in matter around us."

Nineteen papers were presented at the symposium. Among the titles were these: Fundamental Studies on Corrosion, Corrosion in the Tropics, Mechanism of Inhibition of Corrosion of Iron by Neutral Inhibitions, Corrosion Problems Confronted by the Chemical Industries, Corrosion of Aluminum, Cathodic Protection of Underground and Submerged Steel Structures, Rubber Lining of Chemical Process Equipment, Anti-Corrosive Paints for Ship Bottoms, Organic Processes in the Treatment of Surfaces and Electrolytic Corrosion of C. I. Cylinders Liners in H. S. Diesel Engines.
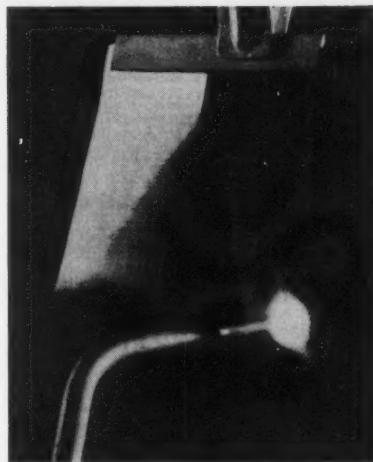
REFRACTORY PROPERTIES of graphite cloth are demonstrated above. An Oxyacetylene flame was passed over a strip of stainless steel mesh (left) and onto a band of graphite cloth of square weave, 28 by 28 construction. With the flame set low on oxygen so as not to oxidize the graphite, the heat quickly melted the steel mesh but caused only an incandescent glow on the graphite cloth which has no melting point at ordinary pressures.

2 Corrosion Papers to Be Given at Design Meeting

Two papers of interest to corrosion engineers will be presented in the materials symposium at the 1959 Design Engineering Conference to be held May 25-28 at Convention Hall, Philadelphia, Pa. The conference is sponsored by ASME.

The two papers are "Latest Developments in Materials to Resist Chemical Corrosion" by S. W. Shephard, Chemical Construction Corp., New York City, and "Latest Developments in Materials and Coatings to Resist Atmospheric Corrosion" by E. Burt Friedl, Louis J. Nowacki and William H. Safranek.

Nickel Oxide Samples

A new standard of nickel oxide powder is available from the National Bureau of Standards. Analyzed and certified for nine minor and trace elements, the sample is intended for checking and calibrating spectrochemical and chemical methods employed in analysis of high-purity nickel, particularly electronic-grade and electrolytic nickel.

Samples are packaged in bottles containing 25 grams and are available from the Standard Sample Clerk, NBS, Washington 25, D. C. The fee is $8.00 per sample.

Venezuela Consul in Dallas

The Consulate of Venezuela in Dallas, Texas, is located at 1309 Main Street and has office hours on weekdays from 10 to 3.

Chromium-Nickel Coating Prevents

Molybdenum Oxidation at High Temperatures

Abstract

Molybdenum must be protected against oxidation at elevated temperatures. With the composite chromium-nickel coating developed by the National Bureau of Standards for the Navy Bureau of Aeronautics, oxidation is prevented for over 1000 hours at 980 C. The coated molybdenum, which is produced by electrodepositing nickel over chromium, promises to be useful in turbine blades and similar high-temperature components.

5.3.4

TO PROTECT molybdenum against high-temperature oxidation, the National Bureau of Standards, in research performed for the Navy Bureau of Aeronautics, has investigated a composite electrodeposited coating of nickel over chromium.[1] Although molybdenum has greater structural strength at high temperatures than steel, it has not been used under such conditions because of its ease of oxidation. However, oxidation of molybdenum is prevented for over 1000 hours at 980 C and for over 300 hours at 1100 C. The two-layer coating is considered a promising material for use on turbine blades and similar high-temperature components.

A high-temperature coating for molybdenum must have a number of special properties. It must be oxidation-resistant, non-porous and ductile. Minute imperfections can allow molybdenum beneath the coating to oxidize completely within a few hours. Studies of the chromium-nickel coating show that, if properly applied, it satisfies these requirements.

First step in the plating procedure is to etch the molybdenum with a 1:1 solution of concentrated sulfuric and phosphoric acids. A 1-mil chromium deposit is electroplated on the molybdenum at 85 C and 120 amp/dm². Then the newly plated surface is again etched, this time with a 1:1 hydrochloric acid, given a nickel strike and plated with 7 mils of nickel. For this purpose, nickel deposited from a Watts type bath at 2 to 5 amp/dm² is superior to that deposited from an all-chloride bath.

Durability Studies

Several durability experiments were conducted with the coated samples. Completed specimens were bent until fractured to test coating adhesion. The break produced was usually within the molybdenum itself and not between the electrodeposited layers—showing excellent adhesion of the plating. Soundness of the deposit largely determines the effectiveness of protection.

Specimens with the composite coating were exposed to air at 1100 C until the coatings were perforated or until a white smoke of molybdic oxide appeared. At this temperature the coating withstood oxidation for an average of 300 hours, but at 1200 C oxidation was greatly accelerated. Preheating of the samples in an inert atmosphere decreased the oxidation life of the coatings.

Supplementary Information

In metallurgical examinations of a series of the coated specimens which had been subjected to different periods of air oxidation at 1100 C, three under-
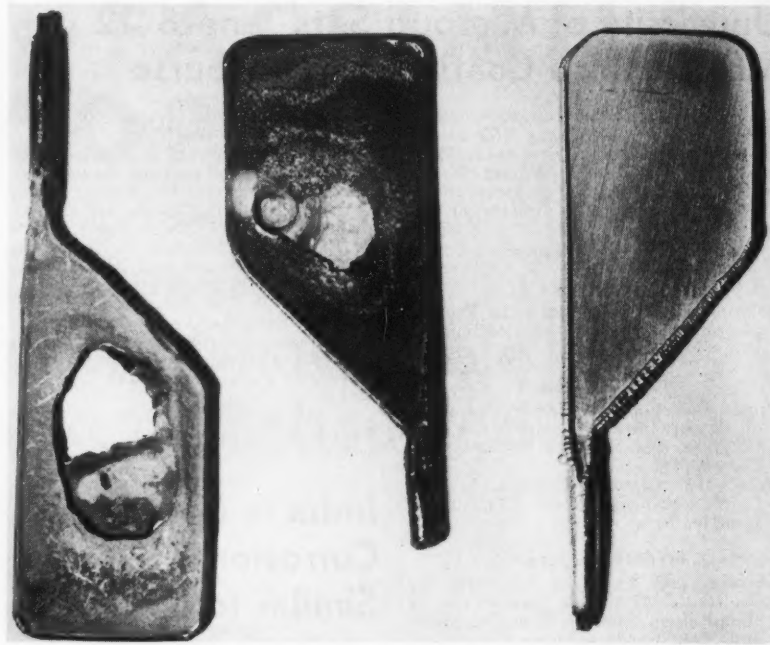
MOLYBDENUM TEST PANELS coated with composite chromium-nickel coating developed by the National Bureau of Standards. Panel on the left was not heated. The other two were heated 300 hours at 1100 C. Difference between the two heated samples shows the variation in samples prepared under identical conditions.

lying causes of failure were noted: subsurface oxidation, grain-boundary oxidation, and edge separation.

Subsurface oxide is due to reaction with atmospheric oxygen and not with oxygen trapped in the coating. This explanation is plausible because the oxide was not observed in samples heated in a helium atmosphere. Apparently the subsurface oxide layer is caused by diffusion of the atmospheric oxygen which passes through the nickel coating and reacts with the nickel-chromium alloy underneath. Further support of this explanation is the fact that the low-chromium alloy is more easily oxidized than is pure nickel. The subsurface oxide forms through much thicker layers of nickel over a curved than over a flat surface.

The boundaries of the metal crystals are more vulnerable to oxygen attack. Grain-boundary oxidation directly follows the boundary of the grains.

Edge separation occurs within the chromium-nickel diffusion layer when a sample is alternately heated and cooled several times. This type of defect actually produces a gap within the layers.

To observe more closely the effect of molybdenum diffusing through the coating, a study was made also of interdiffusion of the three metals—molybdenum, chromium, and nickel. For this experiment, a bar of molybdenum was plated with 2 mils of chromium and 14 mils of nickel and then heated in hydrogen. After 600 hours, 1 to 2 percent of the

molybdenum had diffused to the surface. Although this metal could be detected through 10 mils of nickel, no structural changes were noted. Apparently small amounts of molybdenum which diffused into the surface do not affect the grain structure of the chromium-nickel alloy coating.

In other investigations of the three types of defects, electroformed nickel instead of molybdenum was coated with chromium and nickel and then oxidized. Upon examination, the same three formations—subsurface oxide, grain oxidation and edge separation—which had occurred with the coated molybdenum, were noted. Thus, molybdenum itself is not directly involved in these major sources of failure.

[1] For further technical information: Protection of molybdenum from Oxidation at elevated temperatures. D. E. Couch, H. Shapiro, J. Taylor and A. Brenner, *J Electrochem Soc*, **105**, 450 (1958).

Atomic Energy Meeting

The Second Annual Texas Conference on Utilization of Atomic Energy will be held at Texas A & M College November 12-13. It will be devoted to presentation and discussion of papers on atomic energy applications. Topics will include nuclear reactors, radioactive isotopes, thermonuclear power and other aspects of the atomic energy field.

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Two New Plastics Can Be Used as Metal Substitutes

Two new plastics expected to have a substantial impact on industry have been developed by American Potash and Chemical Corp. and E. I. duPont de Nemours & Co. American Potash's phosphinoborines are based on boron and phosphorus instead of silicon-oxygen combinations. DuPont's "Deldrin" acetal resins (polyoxymethylene) are thermoplastics developed primarily for use in fields now dominated by die-cast metals. Deldrin's starting point is formaldehyde, which is formed into a linear polymer with no side branches.

The phosphinoborines, as reported at a national meeting of the American Chemical Society by Dr. Ross I. Wagner and Frederick F. Caserio, Jr., ultimately will be developed to withstand temperatures to 400 C (750 F) and have other characteristics suiting them to be substituted for metals. The two basic types developed so far are a milky-white compound which is heat stable but brittle and another which is more like conventional plastics but does not have heat stability. Further research will be conducted seeking to combine the two characteristics.

DuPont's material, which will be available commercially about midyear, is reported to be extremely rigid without being brittle, is 80 percent lighter than zinc but twice as costly per cubic inch. Principal uses are seen in components for automobiles, plumbing and consumer products, over 75 percent in replacement of metals. Field tests show the material resists 180-degree water and hot air indefinitely without bad effect.

Although Deldrin in terms of yield per pound costs twice as much as zinc and more than twice as much as aluminum, it is expected to be a strong competitor when extensive finishing is required. In automobile applications for example, it can operate for long periods at temperatures to 250 F and has excellent resistance to gasoline, motor oil, brake fluid, alcohols, glycols, ketones, esters, aldehydes and ethers.

When used for such things as shower heads, Deldrin plastics operate at temperatures far too high for comfortable bathing and will neither corrode, build up calcium deposits nor stain from rusty water.

Robots Respond to Sound, Perform Human Functions

Mechanical robots which respond to sound and perform many human functions have been designed by Babcock & Wilcox Company's Atomic Energy Division at Alliance, Ohio. The automatons are being designed to perform reactor maintenance and repair operations in radiation fields too hot for humans.

Largest and most complex of the robots is a 3-ton, 8-foot fork-lift truck with three arms especially adapted for functions they will perform. One arm will be able to duplicate many human wrist and arm movements, the other two arms will be able to lift a small wrench of a 1000-pound object 15 feet in the air.

Railroad Conference

Corrosion Effects on Railway Equipment, a paper by E. A. Foster of the Association of American Railroads, was presented last month at the second railroad conference sponsored by ASME and AIEE in Chicago.

Sodium Corrosion Paper

Sodium Corrosion as a Function of Time, a paper by J. M. McKee of the Nuclear Development Corporation of America, was presented at the Fifth Nuclear Congress held last month at Cleveland, Ohio.

Sea Horse Institute Sets Meeting for June 1-5

The Sea Horse Institute will hold its annual meeting June 1-5 at Wrightsville Beach, N. C. A list of topics proposed for discussion has been mailed to members. The topics most popular with the members will be discussed.

Inspection trips are planned at the Kure Beach atmospheric exposure racks and the Harbor Island Corrosion Test Site adjacent to Wrightsville Beach.

Hotel accommodations should be sent to T. P. May, P. O. Box 262, Wrightsville Beach, N. C.

International Conference On Common Language Is Set

A 3-day international conference entitled "Standards on a Common Language for Machine Searching and Translation" will be held September 6-12 in Cleveland, Ohio.

Sponsored by Western Reserve University and Rand Development Corporation, the conference is proposed to encourage development of a common machine language or a series of compatible machine languages to prepare scientific and technical literature for searching, selecting, correlating and translating by automatic equipment.

Additional information is available from the Secretariat, Center for Documentation and Communication Research, Western Reserve University, Cleveland 6, Ohio.

Gas Chromatography Gives Greater Product Purity

Greater purity in petrochemical and petroleum products will be possible through advances in the science of gas chromatography, according to Gulf Oil Research Laboratories.

Impurities of less than 1/100th of one percent in a drop of liquid can be detected and isolated for examination by other devices. These advances are expected to clarify the composition of many materials and to give purer products more exactly tailored for their intended uses.

BOOK NEWS

Atomic Industrial Progress and Second World Conference: July-December, 1958. United States Atomic Energy Commission. 386 pages. 6 x 9 inches. paper bound. Available from Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. Single copy price $1.25.

Discusses the growth of industrial atomic energy uses in 1958 in such fields as power reactor technology, radioisotopes, biomedical assistance to atomic industry and international industrial progress. Also gives highlights of the Second World Conference on Peaceful Uses of Atomic Energy and surveys major activities in atomic energy programs.

Annual Report for 1957—European Federation of Corrosion and its Member Societies. Available from the General Secretariat of the European Federation of Chemical Engineering, Frankfurt (Main) Office, Dechema, Rheingau-Allee 25, Frankfurt, Germany. 147 pages. Single copy price for non-members DM 30. Prepared by the General Secretariat of the European Federation of Corrosion.

The 8½ x 1½-inch paper bound volume is printed in French, German and English. The three parts give reports on the federation, reports of the member societies and a survey of research institutes which are concerned with corrosion problems and the protection of materials.

Research at Case—1958. Case Institute of Technology, University Circle, Cleveland 6, Ohio. 8½ x 11 inches, spiral bound. Distributed free to industrial associates of Case and other interested persons and organizations. Published January, 1959. Available from Development Office or Coordinator of Research.

A publication of references to research projects in progress at Case Institute during the past year, to theses completed by graduate students and to scientific and scholarly works published by the faculty and staff.

Steel Cleaning Techniques Discussed in Navy Books

Two Navy publications on cleaning techniques for corrosion resistant steel are available from the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C., at 75 cents each.

"Cleaning and Passivation of Corrosion-Resisting Steels (PB 131964) surveys typical cleaning methods for removing surface contaminants such as scale, flux, slag, metallic lubricant and iron from steels and discusses the function of passivating treatments in nitric acid solutions as a final cleaning operation.

"Effect of Halide Addition to the Sulfuric Acid Pickling Bath" (PB 131-794) discusses the fact that sodium halide additions to standard sulfuric acid pickling bath reduces acid attack on base metal, especially for special treatment steel.

Small Atomic Generator Wins Miniaturization Award

The 1958 Miniaturization Award was given to the Nuclear Division of the Martin Company, Baltimore, Md., for development of Snap-III, a 5-pound atomic generator capable of producing power during its lifetime equivalent to the power produced by dry cell batteries 300 times its weight.

Established in 1957 and sponsored by Miniature Precision Bearings, Inc., Keene, N. H., the award is given annually to recognize advances in the art and science of miniaturization.

AEC Awards 440 Contracts

The Atomic Energy Commission awarded 440 unclassified research and development contracts in physical sciences to colleges, universities, private research institutions and industrial firms during 1958. Of these, 205 contracts were in the field of chemistry awarded to 89 institutions, 105 in metallurgy to 61 institutions, 101 in physics to 55 institutions and 19 in controlled thermonuclear research to 17 institutions.

Battelle Reactor Operates At Doubled Power Level

Power level of Battelle Memorial Institute's research reactor has been doubled, raising its normal operating level to two million watts. The reactor has just completed its first full cycle of 12 days of continuous operation.

Plans are being made to establish a laboratory designed especially for studies of plutonium. It will be located at the Nuclear Center, where the reactor and hot cell and critical assembly facilities are in operation.

Iron Corrosion Symposium To Be Held November 5-7

A symposium on the corrosion of iron and tin in contact will be held as part of the Southeastern Region Meeting of the American Chemical Society, November 5-7 in Richmond, Va.

Papers will be accepted for presentation at the meeting until August 1. Papers on such topics as effect of metal ions on the corrosion of iron and tin, polarization curves for iron and tin, oxide films on iron and tin, corrosion inhibition and the theory of corrosion of metals in contact will be considered.

Additional information can be obtained from the symposium chairman, Henry Leidheiser, Jr., Virginia Institute for Scientific Research, 2820 Grove Ave., Richmond 21, Va.

Aluminum

Interlocking Linings made of aluminum for boxcar interiors, called Reynolds Inner Liners, cut in half the lining weight over steel. Extruded by the Reynolds Metal Company at its Grand Rapids, Mich., plant, the liner components can be removed and re-used if the boxcar is retired or damaged. The welded-in method is replaced by extruded aluminum clips that fasten the liners to the wall with blind rivets.

Aluminum Tubes for condenser and heat exchanger applications are being produced by Bridgeport Brass Co., Bridgeport 2, Conn. The tubes will be made in a range of alloys in all commercial sizes.

Ceramics

LV Series Pumps, their capacities, applications and construction are described in a brochure available from General Ceramics Corp., Keasbey, N. J.

Farbo-Tile, a vitreous glaze finish for brick, concrete, dry wall, hard-board, cinder block and plaster has been introduced by Farboil Company, 801 Key Highway, Baltimore 30, Maryland. It is a permanent surfacing material designed to simulate glaze tile's performance and appearance. It is applied by spraying and is resistant to abrasion, stains, acids, alkali and solvents and is available in several colors.

I-C Insul-Sure molded Fiberglas pipe-fitting insulators are being produced by Insul-Coustic Corp., 42-23 54th Road, Maspeth 78, N. Y. They are installed by placing the two halves over the pipe fitting and joining them by wire, staples or tape. They are available in 1- and 1½-inch thickness to fit most standard welded and screwed fittings from ½-inch thickness to 8 inches.

Brick Floor Installation featuring the preparation of corrosion and wear resistant joints is illustrated and explained in a bulletin available from Master Builders Company, Cleveland 3, Ohio. The method described uses Embeco mortar which is claimed to counteract all mortar shrinkage.

Change of Address

Babcock & Wilcox Company has moved its tubular products district sales office to 464 Peachtree Bldg., 805 Peachtree St., N.E., Atlanta 8, Ga.

Farwest Corrosion Control Corp., has moved into a new building at 1837 Pontius Ave., Los Angeles 25, Cal.

Coatings—Organic

Test Samples of Isophthalic-based alkyd and polyester resins are available to resin and paint manufacturers for evaluation and testing from Oronite Chemical Co., 200 Bush St., San Francisco 20, Cal. Supplied with technical data on each resin, the samples are provided to assist chemists in developing their own resin formulas.

Corrosion Resistant Coatings, Bulletin No. 249, is available from Wisconsin Protective Coating Corp., Green Bay, Wis. Specifications are given on 17 Plasite coatings.

Kupl-Koter, a new pipe coupling made by Dresser Manufacturing Division, Bradford, Pa., is designed to give quick, uniform field coating of pipe couplings. The couplings consist of two halves, each with a sponge rubber gasket cemented in a groove in the leading edge. They are clamped together with slip-on clamps with steel bands drawn tightly at each end. They will handle coatings at recommended pouring temperatures.

Satin Black, a new coating that adheres to galvanized iron, aluminum, brass, plastic, glass, magnesium and stainless steel has been introduced by Southern Lacquer & Paint Corp., South Gate, Cal. The manufacturer states that when Satin Black is used as a primer it may be re-coated in 20 minutes with any conventional paint, enamel or lacquer. It does not need thinning and can be used as received for spray or dip application.

Urethane Coatings produced by the Polly Form Manufacturing Co., Escondido, Cal., are described in literature available from the company. Included is a new glass-like coating to be used instead of paint. It can be brushed, sprayed, rolled or dripped on wood, concrete, metal, fiberglass, fabrics, etc. It has resistance to heat, abrasion, rust, marine corrosion, sun, chemicals, oil, moisture, acids, gases, etc.

Drilling Services

Layne Texas Drilling Service, 5402 Lawndale, Houston, Texas, is drilling 28 and 30-inch cavern storage and brine wells. The company offers services, tools and controls to complete these large diameter wells. Forty-inch mine shafts and air shafts for 36-inch pipe have also been drilled. Services include drilling and cementing the casing for the large holes.

Fittings

Smith Split-Coupling, made by Pipe Line Development Co., 5700 Detroit Ave., Cleveland 2, Ohio, is designed for pipeline repairs and can be used as a coupling, split sleeve or pipe repair clamp. Made of steel, it can be welded as an integral part of the line while the pipeline is in service.

Self-flaring Tube Fittings have been developed by the Flodar Corp., Cleveland. They employ a hardened steel sleeve to press the tube into the contoured body to form a flare as the fitting is tightened. They are available in steel, stainless steel, brass and aluminum.

Gaskets

Guardian Spiral Wound Gaskets made of metal are described in a new bulletin published by Garlock Packing Co., 434 Main St., Palmyra, N. Y. The gaskets consist of spirally wound strips of V-shaped preformed stainless or zinc coated carbon steel alternated with layers of asbestos or Teflon. They are recommended for service use against gases and liquids including most chemicals in high pressure, high temperature applications.

Heaters

Non-Corrosive Hot Oil in welded piping has been used to keep 58,000 square feet of concrete entrances to Chicago's Calumet Skyway Bridge free of snow. Concealed beneath the concrete, the hot oil pipes heat the roadway to 34 to 36 F to keep the 22-lane tool plaza area free of ice and snow.

Inhibitors

Entek 45, a liquid additive to hot water rinses to prevent spotting and subsequent corrosion of metals, has been developed by Enthone, Inc., New Haven, Conn., subsidiary of American Smelting and Refining Company. The additive helps shed rinse water rapidly from metal surfaces to give faster drying and elimination of water spots and stains.

No-Wrap Rust Inhibitor Discs have been developed by Chippewa Paper Products Co., Inc., 2425 S. Rockwell St., Chicago 8, Ill. The discs are impregnated with volatile corrosion inhibitor which slowly vaporizes to form a corrosion preventing film on steel items being packaged. Available in round, square, oblong and triangular discs, each shape contains a different amount of inhibitor for bag volumes from 50 to 350 cubic inches.

Insulators

Fluorglas, a Teflon coated glass fabric used for electrical insulation, no-stick coatings and in heat sealing applications, is described in a folder available from Commercial Plastics & Supply Corp., New York City, and its branches in Newark, N. J., Philadelphia and Pittsburgh, Pa., Miami, Fla., and Greensboro, N. C. The folder includes information on five types of Fluorglas fabrics, adhesive tapes, yarn, thread and lacing tape.

Casing Insulator Style 115 has been introduced by Dresser Manufacturing Division, Bradford, Pa. It is designed to protect carrier pipe from crossing casing and to facilitate pipe installation. Its special shape minimizes drag friction when carrier pipe is threaded through casing and reduces any tendency for the insulator to slip on the carrier pipe, thereby damaging pipe coatings.

Slip-Over UPVC Couplers to prevent corrosion caused by flow of stray cur-

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NEW PRODUCTS

(Continued From Page 114)

rents at natural gas distribution piping service connections to customers' homes have been developed by Tube Turns Plastics, Inc., Louisville, Ky. The fitting is an insulating connection of inert, non-conducting, high-impact unplasticized polyvinyl chloride. It has gaskets that grip the pipe ends when the coupling is tightened and a sliding spacer ring of UPVC that is inserted to keep the pipe ends from making contact with each other inside the coupler.

Laboratories

Newly Built Lecture Hall for the advancement of scientific learning has been opened at Shell Development Company's Emeryville, Cal., Research Center. The 295-seat hall will be used for lectures and seminars.

•

Temco Aircraft Corporation is building a new 52,500 square foot Engineering Center for expansion of existing laboratories, spectrograph room and dust-free, climate-controlled areas for electronics and missile systems. The new center will be located along Jupiter Road in Garland, Texas, adjoining the Dallas city limits.

•

Electrochemical Research and development activities are being expanded by Metal & Thermit Corporation. The new facilities to be located in suburban Detroit will house expanded research programs in chromium, copper, nickel and tin plating.

Lubricants

Two Anti-Friction Lubricating Compounds said to have no melting or dropping point are described in a new folder published by Whitmore Manufacturing Co., Cleveland 4, Ohio. Test data and performance characteristics are given of interest to earth-moving, mining, quarrying, processing and manufacturing industries. The lubricants are designed to provide constant protection to roller, ball and sleeve bearings or sliding surfaces in hot bearing applications or in areas with high ambient heat.

Metals—Ferrous

Union Supply Company, Durham, N. C., is now distributing 4-D wrought iron for A. M. Byers Co., Pittsburgh, Pa.

•

Bolton Special Stainless Steel, a new metal alloy combining and retaining the mechanical properties essential to Jordan refining in the paper industry, has been developed by John W. Bolton & Sons, Inc., Lawrence, Mass. It is a chrome-nickel alloy containing about the same chrome and nickel content as AISI 300 Series Stainless. The manufacturer states that the metal combines wear resistance and corrosion resistance where previously one had to be sacrificed for the other.

•

Condulets for Corrosive Locations is the title of a bulletin (No. 2699) giving corrosion resistant properties, applications and descriptions of conduit manufactured by Crouse-Hinds Co. The bulletin is available from the company at Syracuse 1, N. Y.

Wrought Iron, manufactured by A. M. Byers Co., Pittsburgh, Pa., is being used for electrical conduit in a trenched area under the Harlem River in New York City. City specifications required material capable of resisting many years of corrosive attack under water.

Metals—Non-Ferrous

Iochrome, a new 99.997 percent pure chromium metal available from Chromalloy Corp., 450 Tarrytown Road, White Plains, N. Y., is described in a bulletin offered by the company. Produced by an iodine decomposition process developed by Battelle Memorial Institute, the metal contains no single metallic or gaseous impurity in quantities greater than 10 parts per million. The bulletin includes suggested applications, typical analysis, photos showing fracture and fabricability characteristics and a chart which compares the new alloy's fabricability to electrolytic chromium when chromium-nickel alloy sheets containing each are rolled at various temperatures.

Non-Metallics

Manufactured Graphite is being produced in flexible fiber and fabric form by National Carbon Co., Division of Union Carbide Corp., 30 E. 42nd St., New York 17, N. Y. The new graphite form was developed by a new process that converts organic textile forms directly to graphite with a purity above 99.9 percent. Any textile form—yarns, braids, felts or woven and knit fabrics can be produced. At ordinary pressures, graphite has no melting point and sublimes only at extremely high temperatures.

•

GRB Silicon Carbide (silicon carbide bonded graphite), a light weight material with high thermal shock and erosion resistance, is now in pilot plant production at the Carborundum Company's New Products Branch at Niagara Falls, N. Y. The new super refractory material may have possible applications in rocket nozzles, missile leading edges, nose cones and similar uses. Its specifications include light weight (2.3 to 2.8 gms per cc), transverse strength 7000 to 16,000 psi at room temperature and 5000 to 12,000 psi at 2550 F. It also has resistance to oxidation, erosion and thermal cracking.

Painting Equipment

Catalog covering new and improved spray equipment is available from De-Vilbiss Co., Toledo 1, Ohio. Included is information on 15 different models of spray guns, air compressors, air regulating equipment, paint cups and tanks, spray booths, exhaust fans, hose and connections, infra-red drying equipment, hot spray units, respirators and underbody coating equipment.

Pipe Putty

Scotchrap, a new pipe putty designed to eliminate sharp corners on pipe fittings before application of pipe protection tape, is being produced by Minnesota Mining and Manufacturing Co., Dept. D9-108, 900 Bush Avenue, St. Paul 6, Minn. The new compound was designed to make the taping of irregular shapes such as tees and couplings better and easier. It provides a smooth taping surface that helps eliminate wrinkles and buckles in the tape.

Plastics

Teflon-Coated Cups for use in hydraulic and pneumatic equipment has been developed by Garlock Packing Co., Palmyra, N. Y. The cups are designed to reduce the break-away torque required to operate cylinders. They help reduce running friction and are reported not to stick to cylinder walls even after prolonged idle periods.

•

Estane VC, a new rubbery plastic material that snaps back like rubber but works without vulcanizing has been developed by B. F. Goodrich Company's Research Center, Brecksville, Ohio. It resists tearing and the effects of abrasion, solvents, oil and ozone. When deposited in film form from a solvent, it has a tensile strength of 7000 to 8000 psi. This film can be re-dissolved in the specific solvent and re-deposited as another film with equal properties. The new product is in production at the Avon Lake (Ohio) Development Center of B. F. Goodrich Chemical Co.

•

Fusion Welding, a new Teflon fabrication technique, permits assembly of one-piece lengths or configurations of the material at reduced costs, according to United States Gasket Co., Camden 1, N. J., plastics division of the Garlock Packing Company. The resultant weld is a pure fluorocarbon with the same heat, chemical and electrical properties of Teflon, with good tensile strength and elongation.

•

PL-12 Plastic, a new acrylic-type thermoplastic polymer possessing high heat resistance and exceptional combination of stiffness and toughness, has been developed by the J. T. Baker Chemical Co., Phillipsburg, N. J. It has a heat distortion point of 240 F, a flexural modulus of 415,000 psi and a notched izod impact strength of 1.0 ft/lb/inch. Injection molding and extrusion can be carried out by conventional acrylic techniques, according to the company. The natural resin is straw-colored and has fair transparency.

•

Dur-X, a plastic drain pipe that conforms to trench beds and contours, is described in a brochure available from Franklin Plastics, Inc., Franklin, Pa. Its weight is approximately ⅛ that of ordinary cast iron pipe and is available in 10-foot lengths in sizes from 2 to 6 inches. It is designed for use in foundation drainage, septic tank systems, industrial non-pressure waste disposals and for reclaiming swampy areas.

Process Equipment

Ejector Equipment for the process industries is being made of a variety of corrosion and abrasion resistant materials. These include cast iron, bronze, special alloys, titanium, lead and non-metallics such as ceramics, plastics, stoneware and porcelain. Ejector equipment designed for special applications and made of these corrosion resistant materials is available from Schutte and Koerting Co., Cornwells Heights, Bucks Co., Pa.

Now you can predict service life because Byers PVC Pipe Engineering brings a factual approach to piping system design

FACT: Extensive testing program is basis for working pressure recommendations

Laboratory and field experience have shown that it is absolutely essential to test the extruded pipe to determine its physical properties.

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Our recommended pressures are usually about 10% of burst pressure rather than the frequently recommended 20%. Safely below the creep range, our values are dependable. That's why you should consider Byers PVC Pipe—Type I or Type II—for your plant services. Call our field service representative for the entire PVC story. **A. M. Byers Company, Clark Building, Pittsburgh 22, Pa.**

RECOMMENDED WORKING PRESSURE VS TEMPERATURE
TYPE I PVC - PLAIN END
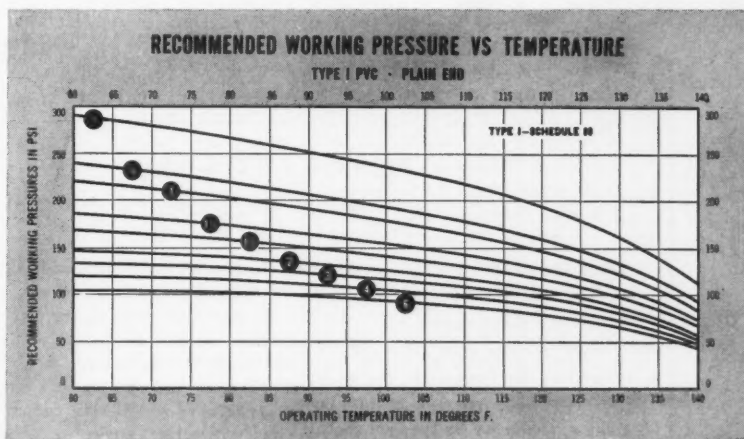
To convert our test results into good design practice, you must consider static test loads vs. installed dynamic loads—the experimental variation and the indeterminate loads of actual operation.

Ⓑ BYERS PVC PIPE

ALSO SHEET AND ROD STOCK

Write our Engineering Service Department for copy of this new 32-page illustrated catalog on Byers PVC Pipe.
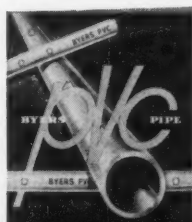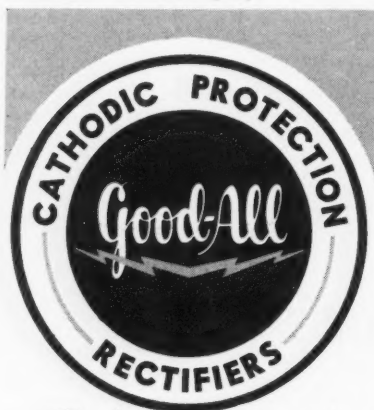
Schools

Spray Painting Schools are being held until June by the DeVilbiss Company, Toledo, Ohio, for the 36th year. Each session is five days and includes both theory and practice of spray painting. No fee is charged, and all equipment and materials are furnished. The schools are open to all owners and sellers of DeVilbiss equipment or their representatives and operators. Field schools have been held or are scheduled for three west coast cities plus Salt Lake City, Dallas, Kansas City, Ft. Scott, Kan., St. Louis, Chicago, Atlanta and Springfield, N. J.

Silver

Industrial Uses of silver accounted for over half the estimated 250,500,000 troy ounces of silver consumed in the free world during 1958. Industrial uses are expected to expand so that traditional use of silver in the arts will be less important to silver producers as an outlet, according to American Smelting and Refining Co., 120 Broadway, New York 5, N. Y. Largest use of silver is the photographic field for sensitized paper and film. Second most important industrial outlet is for silver solders for brazing or bonding practically all non-ferrous metals, alloys, iron and steel.

Storage

Controlled Humidity is part of the design of a new warehouse being built by Taylor Fibre Co., Norristown, Pa., for storage of vulcanized fibre under regulated humidity conditions. The warehouse will thus help retain fibre quality improvements effected by the company's dryer used to regulate humidity and temperature for more exacting control of vulcanized fibre properties.

Zirconium

Zirconium Fusion Crucibles, their prices, characteristics and other specifications are given in a brochure available from Oregon Metallurgical Corp., P. O. Box 484, Albany, Oregon. Typical resistance of the crucibles to attack during sodium peroxide fusions is shown in tabular and graphic form.

MEN in the NEWS

Cloyd L. Betzer will be the new technical manager at the Pfaudler Co., a division of Pfaudler Permutit Inc., Rochester 3, N. Y.

•

C. W. Smith has been appointed head of the organic chemistry department at Shell Development Company's Research Center, Emeryville, Cal.

•

Clyde Williams, metallurgist and former president of Battelle Memorial Institute, was awarded the James Douglas Gold Medal of AIME for distinguished achievement in non-ferrous metallurgy.

•

Edward A. Yorkgitis has been appointed a group leader in the chemical research and development department of Hagan Chemicals & Controls, Inc., P. O. Box 1346, Pittsburgh 30, Pa.

•

L. L. Whiteneck, immediate past president of NACE, is now with the Los Angeles Harbor Department, P. O. Box 151, San Pedro, California.

•

Lester Sanders has been promoted to general office manager of the Houston headquarters for Nowery J. Smith Company.

•

Robert D. Stout, head of the metallurgy department at Lehigh University, received the 1959 David Ford McFarland Award for achievement in metallurgy, given by the Penn State Chapter of ASM.

•

Carpenter Steel Company, Reading Pa., has appointed **Robert P. Uhl** to head the sales of the Bridgeport, Conn., area. **Robert A. Kokat** is now district sales manager for the Philadelphia area. **Aldridge E. Hunt, Jr.,** is sales manager for the Hartford, Conn., and Providence, R. I., areas.

•

W. F. Brockwell and **R. O. Barlen** will represent Ladish Co., Cudahy, Wis., at the company's new sales office in Dallas, Texas, Room 1010, 211 North Ervay Building.

•

Robert L. Berwick has been appointed PVC plastic sales engineer in A. M. Byers Company's southeastern division with headquarters in Atlanta, Ga.

•

E. W. Eisenhart has been appointed division sales manager in the central United States for Wilbur & Williams Co., Inc.

•

Thomas H. McGrath will be district sales manager for the Haveg Industries, Inc., new sales and engineering office at 3230 Peachtree Road N.E., Atlanta, Ga.

•

David J. O'Neil, Pasadena, Cal., has been appointed pacific regional sales manager for Carpenter Steel Company. **William C. Kunkelman,** Cincinnati, Ohio, is now mid-western regional sales manager. **Harold R. Potter,** Bay Village, Ohio, is east central regional sales manager.

High Temperature, High pressure

Testing of Organic Coatings
For Oil and Gas Well Tubing*

Abstract

Numerous conditions must be considered in formulating a suitable organic coating for in-hole tubular goods. These conditions include elevated temperatures and pressures, corrosive liquids and gases, physical abuse, distortion and elongation.

Laboratory testing methods to simulate actual operating conditions are discussed, illustrations of test specimens and test data are given.   2.3.7

MANY COATINGS that perform well in tests at atmospheric pressures and ambient temperatures fail quickly when subjected to high pressures and temperatures. This fact led to the purchase and use of an autoclave in which samples of coated metal can be suspended and kept for extended periods at predetermined, closely regulated temperatures and pressures. The autoclave permits using various kinds of corrosive environments surrounding the samples.

The need to determine the performance of coatings destined for use as interior linings for oil and gas well tubing before field exposure caused Plastic Applicators to begin a series of tests, some results of which are given in this article.

Because the environments in oil wells vary over a wide range of liquid contents, temperatures and pressures, it is virtually impossible to assess performance of coatings for use in environments which do not approximate those in the wells. The tests were divided into several subdivisions: One series each at 150 and 200 F, another series at 250 F, 3000 psi, and a third series at 350 F, 5000 psi.

These tests, applied against six generic types believed suitable for oil well environments, were designed to discriminate among these to determine which should be selected for further testing. Some of the generic types were used in different forms, applied by different methods or were modified with other materials. The result was 10 different samples as given in Table 1.

The initial series of test coupons was of the standard flat configuration. Results were indicative of the relative resistance of the coatings material even though they were different from those developed from later tests with tubular specimens.

The environments selected were designed to approximate those that might be expected in oil and gas wells with obvious modification designed to achieve an accelerated reaction. First screening tests were made with water at 150 F with the results shown in Figure 1.

This figure shows that most of the coatings performed well at temperatures of 200 F or less, but that when the temperature was increased to 250 F and the pressure raised to 3000 psi, four of the ten showed some damage. When the

samples were examined after the tests at 350 F and 5000 psi, all but four showed substantial damage. Some failed completely, spalling away from the samples.

Because high pH mud frequently is used in some wells, a series of tests was

made in mud at 13.5 pH. An examination of the results in Figure 2 shows at least two of the coatings had substantial damage at 150 F, four were damaged at 200 F, both at atmospheric pressure.

WATER
150 F

1 2 3 4 5 6 7 8 9 10

200 F

250 F, 3000 psi

350 F, 5000 psi

Figure 1—Tests were made in water at the temperatures and pressures indicated. (Coatings are identified in Table 1.)

HIGH pH MUD
150 F

1 2 3 4 5 6 7 8 9 10

200 F

250 F, 3000 psi

350 F, 5000 psi

Figure 2—Tests in 13.5 pH drilling mud at the temperatures and pressures indicated. (Coatings are identified in Table 1.)

HYDROGEN SULFIDE-WATER MIXTURE
150 F
1 2 3 4 5 6 7 8 9 10
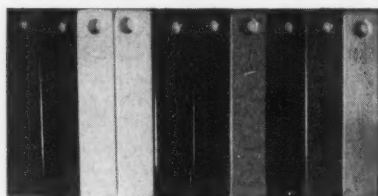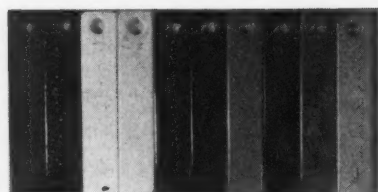
200 F

Figure 3—Tests in hydrogen sulfide-water mixtures at the temperatures indicated, atmospheric pressure. (Coatings are identified in Table 1.)

5% HYDROCHLORIC ACID
150 F
1 2 3 4 5 6 7 8 9 10

200 F
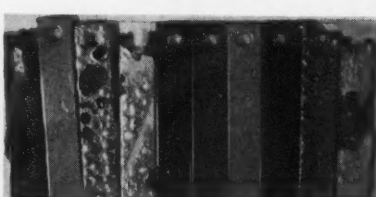
Figure 4—Tests in 5 percent hydrochloric acid at the temperatures indicated. (Coatings are identified in Table 1.)
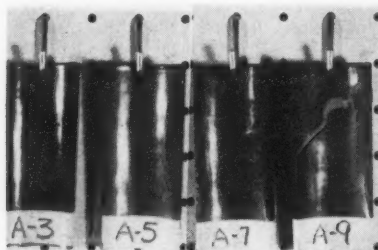
Figure 5—Phenol formaldehyde coatings tested with results indicated in Table 2.

TABLE 1—Types of Coatings Tested
1. Vinyl resin
2. Amine cured epoxy
3. Baked polyeurethane
4. Air dried polyeurethane
5. Phenol formaldehyde
6. Phenol formaldehyde with epoxy modified overlay
7. Epoxy modified phenolic
8. Experimental coating
9. Baked polyamid
10. Air dried polyamid
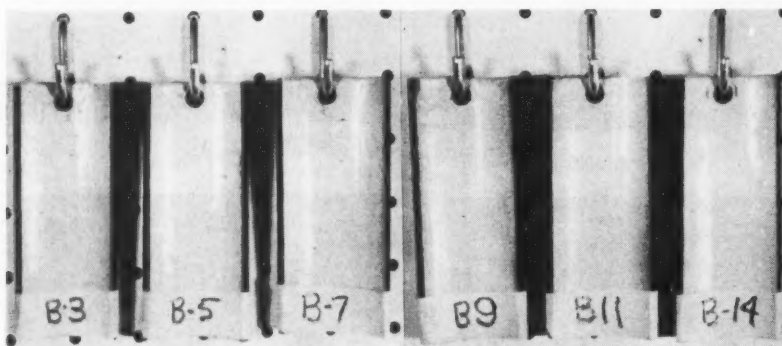
Figure 6—Epoxy modified phenolic coatings tested as indicated in Table 2.

TABLE 2
Results of Tests of Coatings Designed for Application to Oil and Gas Well Tubing
Conditions: Fresh water, 24 hr., 300 F, 6000 psi

Material	3 Mils	5 Mils	7 Mils	9 Mils	11 Mils	14 Mils
Phenolformaldehyde	1	1	6	6	...	...
Epoxy Modified Phenolic	3	1	1	2	4	5
Phenolformaldehyde With Epoxy Modified Overlay	1	1	1	1	3	...

Legend:
1. No change.
2. Tiny blisters.
3. Small blisters.
4. Medium blisters.
5. Large blisters.
6. Cracking and loss of bond.
7. Blistering and loss of bond.

Organic Coatings –
(Continued From Page 121)

When the temperature was raised to 250 F and pressure raised to 3000 psi, two showed substantial damage and others had minor defects. At 350 F and 6000 psi, only three of the ten coatings remained substantially undamaged.

Approximately the same results were obtained with these same coatings tested at like temperatures and pressures in a hydrogen sulfide-water mixture. The results of these tests are shown in Figure 3.

Results of tests run in five percent hydrochloric acid at 150 F and 200 F are shown in Figure 4. The five percent acid solution was used to simulate conditions in a well that was acidized.

These tests accomplished several things. They permitted some of the obviously inadequate materials to be screened out. The tests subjected all materials to conditions more severe than those found in more than 50 percent of all wells using coated tubing today: bottom hole temperatures of less than 200 F and pressures of less than 1500 psi.

Because the number of variations that can be made in a coating or in a combination of coatings is so numerous that it would be economically impractical to test them all under all possible conditions to which they might be subjected, it is necessary to be selective. When necessary, however, extensive tests can be carried out, using this equipment. In one recent case more than 500 different formulations were tested and rejected before a satisfactory compound was found.

One important fact has come to light during the tests made so far: In any final determination of a coating for oil well tubing, it is necessary to use tubular samples. The flat, coupon or barstock samples serve very well for initial screening, but a final test on curved samples is necessary to get usable results.

Some of the results of tests on cylindrical specimens are shown in Figures 5 through 9. These specimens are prepared by taking a cylinder, coating the inside with the proper material at the desired thickness and then curing it. The specimen is then split edgewise before testing in the autoclave. The data are summarized in Table 2.

Figure 5 shows phenolformaldehyde at various thicknesses tested at 24 hours in fresh water at 300 F, 6000 psi. Apparently thicknesses over 5 mils are subject to failure under these conditions.

Figure 6 shows that an epoxy modified phenolic, exposed in the same environment as the samples in Figure 5, reacts in about the same way. Thicknesses over 7 mils show progressive damage as the coatings increase. When a phenol formaldehyde with an epoxy modified phenolic overlay was tested under these same conditions, as shown in Figure 7, performance versus thickness was improved, damage not becoming evident until 11 mils was reached.

Testing of coatings continued uninterrupted. There is no doubt this evidence will make possible a quicker evaluation of coatings for application in specific environments and shorten the time between discovery of a new material and

Figure 7—Phenol formaldehyde with epoxy modified phenolic overlay tested as indicated in Table 2.

Organic Coatings —

(Continued From Page 122)

its application in the field. It has been discovered that a coating tested at 144

hours under conditions approximating those downhole in a well can be expected to give service which correlates well with the results shown in the tests. This saves much time and shortens the period of field testing materially.

Discussion by Robert P. Suman, Pittsburgh Plate Glass Co., Houston, Texas:

Were the pipe sections and coupons displayed in slides checked for holidays with a holiday detector before testing?

Reply by Cordell Garner:

No check was made with the holiday detector prior to testing. Inasmuch as these coatings were checked at varying thicknesses from three mils to fourteen mils, holidays would mean very little in these specific tests.

Discussion by James C. Spalding, Jr., Box 2880, Dallas, Texas:

1. Was water fresh or salt water?
2. What time element was used in screening tests on large number of products?
3. What is criteria of coating failure?

Reply by Cordell Garner:

1. Fresh water.
2. Various, mostly 144 hours.
3. Any indication of failure (blisters, cracking, etc.).

Figure 1—Corrosion Condition in air preheater tubes. Replacement every two years is common practice.
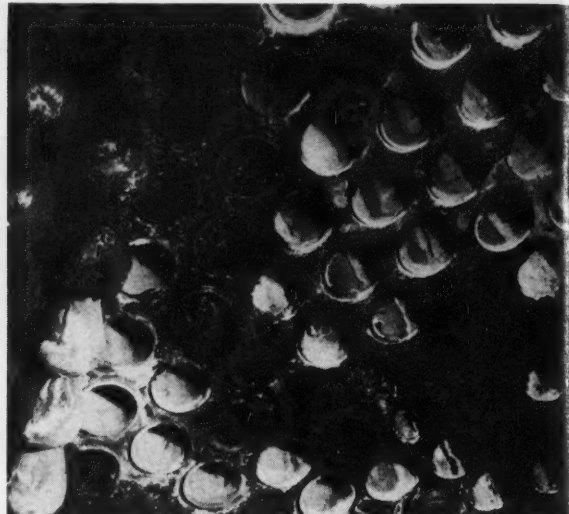
Figure 2—Air preheater tubes and tube sheet showing deposits. Note blockage of left rows of tubes.

Solving Some Oil Ash Corrosion Problems*

Form and Nature of Vanadium

VANADIUM, present in residual fuel oil and in crude oil as a soluble compound and sometimes referred to as a porphyrin, during the process of combustion is oxidized to one of five oxides: V_2O, V_2O_2, V_2O_3, V_2O_4, or V_2O_5 of which the last, the pentoxide, forms salts known as vanadates. Certain vanadium salts yield an intensely permanent black color and are used in the manufacture of inks and for dyeing. Another common use for vanadium is as a contact catalyst in the manufacture of SO_3, making it important in the commercial production of sulfuric acid. It also is used as a reducing agent and as a dryer for linseed oil paints.

Vanadium has been and continues to be obtained commercially from the ash of oil burning furnaces. It is a fairly common practice to chip out slag deposits from furnace floors and boiler uptakes and to extract the vanadium content. Vanadium also is found in other ores mined in the United States, Africa and Peru. Vanadium is difficult to refine into a pure metallic state but fairly easy to make into alloys such as ferrovanadium and nickelvanadium.

Slag and Deposits As Formed

Vanadium pentoxide is reddish-yellow in color. Although it is seldom observed in boiler slag formations to have this appearance, there have been reddish deposits observed on Diesel engine piston heads, which upon analysis have an equivalent to 93 percent vanadium pentoxide. The slag formation from oil-fired boilers generally varies from gray to black in color with some brownish overtones. Analysis of these deposits frequently indicates up to 60 percent vanadium pentoxide. When removed from a cold boiler, the slag is a complex formation containing many other ash-form-

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★ Extracted from a paper titled "Vanadium Corrosion—Cause, Effect and Possible Remedies" by R. S. Norris, R. S. Norris and Associates, Larchmont, N. Y.

ing constituents from the fuel oil, the air and metals of the boiler surfaces. Examination of some slag formations removed from superheater tubes and hangers indicates that they have been in a molten state, having flowed like lava. In its molten state, vanadium pentoxide causes corrosive attack by fluxing with the protective oxide layer on the steel or alloy, leaving bare metal exposed to the oxidation and sulfidation by the sodium, vanadium and sulfur.

Hot and Cold Zone Problems

Sulfur corrosion generally is accepted to be caused by the SO_3 in the combustion products, and the sulfur dioxide may be practically disregarded. Unfortunately however, vanadium is a powerful catalyst for the reaction $2SO_2 + O_2 — 2SO_3$. The gas SO_3 is a severe corrodent in the sulfidation of superheater accessories, and the problem is complicated further by the fact that condensation precipitated at the dew point is extremely corrosive to air preheater tubes and other surfaces in the cold zone. A typical condition of air preheater tube corrosion is shown in Figure 1. For all practical purposes, one might conclude that the dew point of the gases has been raised and that it is the sulfuric acid thus formed which attacks preheater tubes and other components.

Minute concentrations of SO_3 can cause severe corrosion in the cold end of boilers. The percentage of SO_2 converted to SO_3 varies with the sulfur and vanadium content of the fuel. The percentage converted to SO_3 varies inversely versus sulfur. With a fuel of 4 to 5 percent sulfur, only 2 to 4 percent is converted to SO_3; with a 0.1 percent sulfur fuel, some 30 to 40 percent is converted to SO_3. A calculation shows that sulfur corrosion is not a straight-line function of sulfur content of the fuel although all may agree that high sulfur fuels are worse.

Abstract

Vanadium pentoxide and sodium are discussed as some of the elements found in slag deposits which cause corrosion in oil burning equipment. Corrosion problems in the hot and cold zones are considered.

Possible remedies discussed are centrifuging to concentrate the vanadium in a smaller total ash-forming content and additives to raise the melting point of the vanadium. Data are given on fouling and corrosion costs at a station burning 70 million gallons of high vanadium content fuel oil per year.

Depressing the dew point in diesel engine fuel is briefly discussed as a means of preventing the formation of acids so that the sulfur oxides will pass out the stack.

Safety precautions to avoid vanadium poisoning are given for boiler cleaning.
                      4.3.3

Figure 2 shows another phase of the corrosion problem: the deposit formation and blockage of the preheater tubes. This deposit is highly acidic, containing sulfuric and hydrochloric acids. In addition to the corrosion it causes, the deposit also necessitates frequent handlancing of the tubes.

Effect of Sodium

While vanadium has been cited as the element which corrodes metals in the high temperature zone of boilers, gas turbines and Diesel engines, it is not the only one. If it were, corrosion would occur only at temperatures above the melting temperature of vanadium pentoxide, 1274 F. However, many other elements and compounds are in the oil at the time of combustion, and because vanadium pentoxide forms salts known as vanadates, it is unlikely that the pentoxide remains pure in the gas stream long. Uninhibited, sodium vanadates may form which have a melting temperature below 1000 F. For example, a mixture of 75 percent V_2O_5 with 25 percent Na_2SO_4 will melt at 950 F, and SO_3 also is released in the reaction.
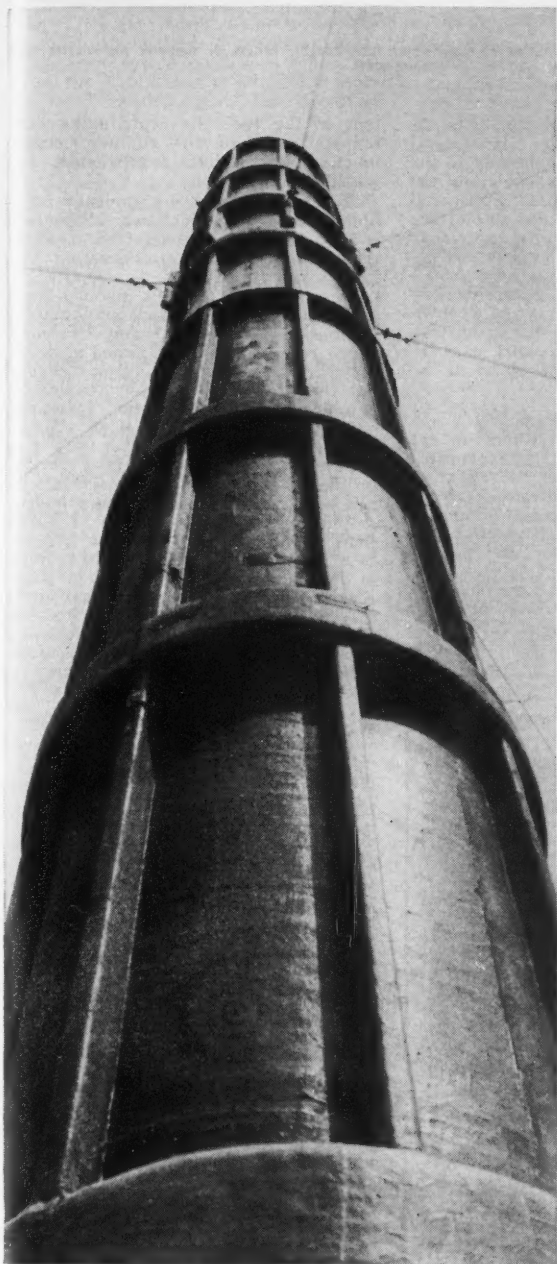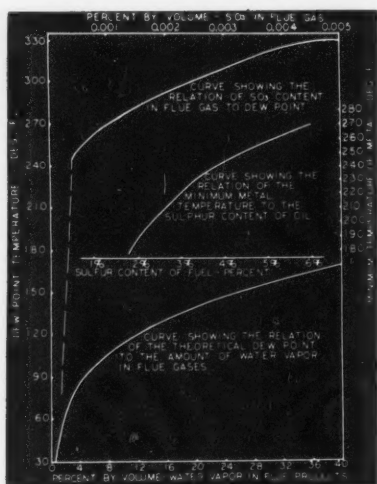
Figure 3—Curves showing the relationship between sulfur in the fuel, SO₃ in the flue gas, minimum metal temperature, and dew point.
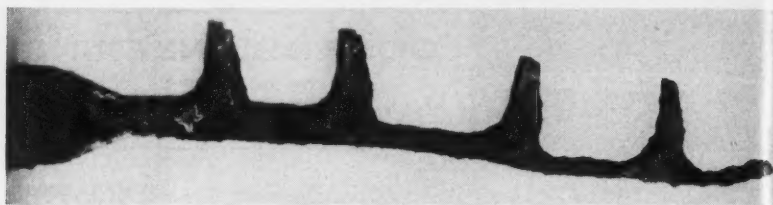

Figure 4—High temperature corrosion of superheater tube hanger. Failure of supports necessitates tube replacements.

Oil Ash Corrosion—

(Continued From Page 126)

The chart in Figure 3 is a family of curves showing the relationship between the sulfur content of the fuel and the minimum metal temperature. Also, the dew point temperatures are shown in relation to the water vapor and the SO_3 content in the flue gas.

Figure 4 shows a typical condition of high temperature corrosion on a superheater hanger which has been wasted away by the sodium and vanadium attack in an oil-fired boiler. This metal wastage does not occur generally to the tubes since they are kept cooler by the steam passing through them. The metal skin temperature of the fire side of the tubes would not normally be more than 75 F higher than that of the steam inside, but the spacers, hangers and baffles are exposed to the prevailing gas temperature. However, since the tubes are cooler, they serve as a better collector on which the vanadates can solidify, and the slag builds up as an insulator.

Some Remedies Explored

Ash content of residual fuel oil can be reduced by centrifuging, but because vanadium is oil soluble, the effect of centrifuging is to concentrate the vanadium in a smaller total ash-forming content. For example, a fuel which before centrifuging may contain 0.057 percent ash of which 8 percent is vanadium pentoxide, after centrifuging may have ash content of 0.036 percent, of which 13 percent is vanadium pentoxide. While this has not reduced the vanadium con-

tent of the fuel, the centrifuging does remove some of the sodium because much of the sodium results from salt water contamination.

So far, there is no economically feasible process by which vanadium and sodium can be removed from fuels at the refinery. Some consideration has been given to removal of ash after oil has been burned, but this involves some form of separator which undoubtedly involves a loss of heat and efficiency. Much research has been aimed at developing an alloy metal which is resistant, but the problem is complicated by the combined influence of the vanadium, sodium and sulfur. Even if an alloy or coating were perfected that was economically feasible, there is a further problem of attack on the refractories and brick work in furnaces and boilers.

Aside from these corrosion problems, there is the problem of fouling and loss of heat transfer and the cost of removal of the deposits formed. Certain trans-Atlantic liners, burning 2500 barrels of fuel oil per round trip, have found it necessary to remove a 10-inch-thick mass of hard, rock-like material from furnace floors with chipping hammers every four trips.

Toxicity Is Serious

For the benefit of anyone who is required to clean out or work in boilers, it may be well to mention a safety precaution. Toxicity of vanadates on humans has been recognized for 70 years. Symptoms of vanadium poisoning include a greenish-black discoloration of the tongue and teeth and a metallic taste in the mouth; irritation of throat and nasal passages with sneezing and an irritating cough; some stomach disturbance and also a skin irritation where sweating occurs.

This poisoning, often referred to as black tongue, usually clears up within 48 hours after withdrawal from the boiler, except that the discoloration of tongue and teeth may persist for four or five days. The minimum protection for the boiler worker should consist of a coverall secured at wrists and ankles, gloves and boots and a hood completely covering the face, provided with an external air supply.

Some Additives Are Effective

Since removal of the oil-ash corrosives before combustion is not practical, the best solution may be an additive in the fuel oil.

Many patents have been issued covering additions to fuel of such inorganic materials as phosphorus, calcium, zinc, magnesium, barium, aluminum, silicon, strontium, zirconium and titanium. In practically all cases, it is disclosed that the function of these inorganic compounds is to raise the temperature at which the vanadium complex melts.

Oil Ash Corrosion —
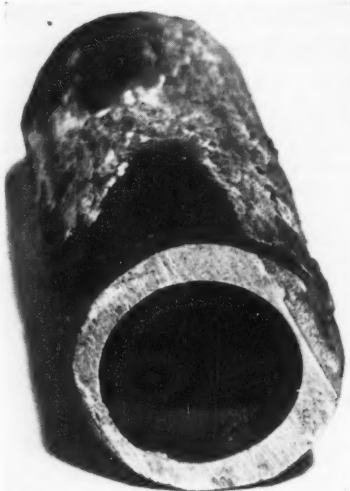
(Continued From Page 128)

Many full-scale attempts have been made to apply such materials as dolomite (CaCO₃·MgCO₃) magnesite (MgO), Epsom salts (MgSO₄) and other similar minerals to the fuel oil. Good success has been reported in some cases while in others fouling, sufficient to cause early shut-down of the boiler, has resulted. While these minerals are relatively inexpensive on a price per ton basis, the equipment required for storage, handling, mixing and injection may be costly.

Supplying a Liquid Additive

Only large central stations of public utilities can justify the capital investment and operating expense needed to apply minerals in the raw state.

Fouling and corrosion costs experienced by a typical central station burning some 70 million gallons of high vanadium content fuel oil per year are given in Table 1.

A liquid, oil soluble and easily applied additive is available which contains a high concentration of metallic compounds in a particle size not exceeding 2 microns which combine upon combustion with the vanadium and sodium to form high melting point vanadates.

Cost of applying an oil-soluble additive in an effective ratio varies with the corrosive content of the oil. However, when applied at a ratio which added about 1⅓ mills $0.0013) per gallon to the fuel cost, or about 5½ cents per barrel of fuel treated, the additive lowered the dew point of the gases through the preheater in such a manner that the extended preheater tube life alone justified use of the additive. Concurrent with this reduction in dew point, it was determined that the SO₃ content of the flue gases was reduced to less than one-half. The relative toxicity of SO₂ compared to SO₃ in the atmosphere is about 1 to 13. For safe industrial hygiene, maximum concentration of SO₃ in the air is 1 mg per cubic meter. For SO₂ the maximum concentration is 13 mg per cubic meter. Obviously, it is desirable to maintain the sulfur in the least obnoxious form. Table 2 gives data on the influence of additives on central station flue gas.

Problem With Diesel Engines

In an internal combustion engine, particularly in Diesels burning heavy fuels, the dew point at the high pressures involved may be 300 F or higher. For this reason, modern Diesel cylinder lubricating oils contain additives of high alkalinity to neutralize sulfuric acids formed.

If an additive in Diesel engine fuel can depress the dew point, acids will not form and the SO₂ and SO₃ will pass harmlessly out of the stack. This is even more probable when it is considered that the dew point in a diesel engine at 1000 psi may be 300 to 350 F. It is entirely possible that depressing the dew point may be more effective at high pressures than at atmospheric conditions.

The gas temperatures immediately adjacent to the cool cylinder wall and piston probably are about 300 F even though the pressure in the cylinder is

800 to 1000 psi and the mean temperature of the charge much higher than the dew point.

TABLE 1—Approximate Cost of Boiler Fouling and Corrosion

	Per Gallon, Cents
Boiler fouling and cleaning, including cleanings necessary before repairs can be safely made	0.15
High temperature corrosion failures of intertube supports, hangers and beams, making superheater replacement necessary	0.44
Low temperature corrosion economizers or air preheaters	0.20
TOTAL	0.79

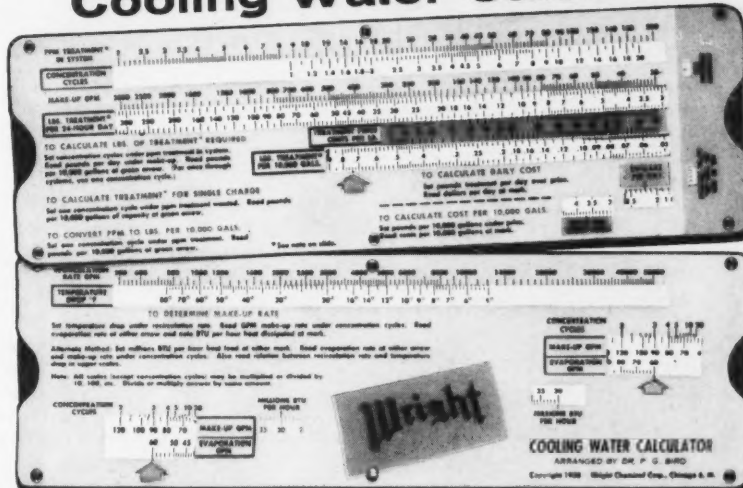**TABLE 2—Influence of Additives on Central Station Flue Gas**

	Boiler Using Untreated Oil	Boiler Using Additive
Acid dew point; degrees F	162.00	125.00
SO₂, percent by volume	0.041	0.071
SO₃, percent by volume	0.0013	0.0006
Sulfur content of fuel	2 percent	2 percent

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Over 40 foreign countries are represented by CORROSION subscribers.

Comparative Effectiveness

Coatings

for

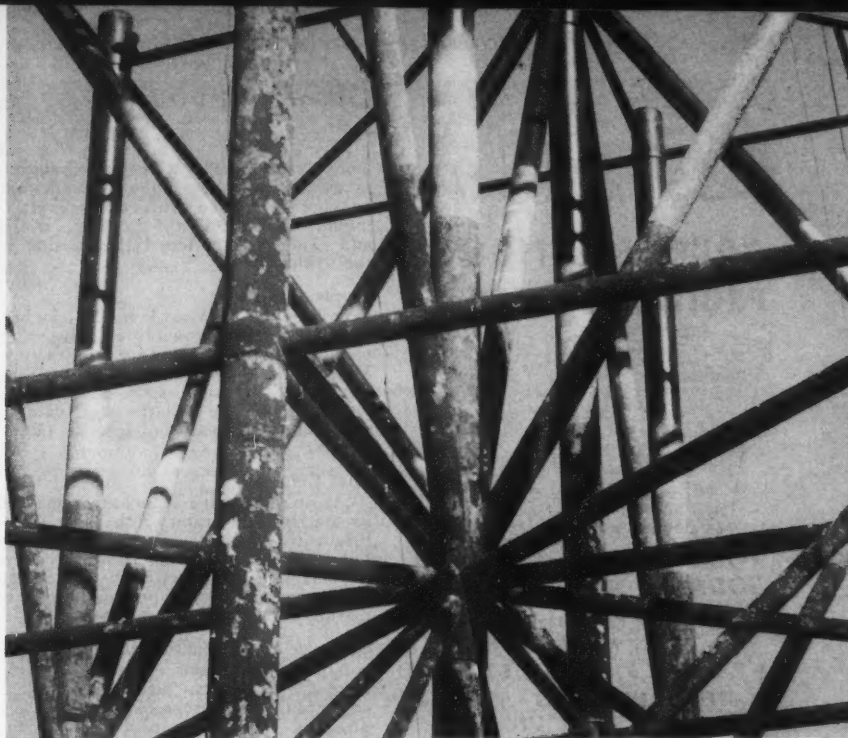# Offshore Drilling

Structures*

Figure 1—Offshore platform jacket with three zones of corrosion protection: upper dark area is organic coating, center light area is Monel sheath and lower area is cathodic protection section.

THREE PRINCIPAL means of corrosion control on offshore platforms are cathodic protection, metallic sheaths where abrasion is maximum, and coatings.

Cathodic protection is used on the pilings below the mean tide level. In the tidal area and splash zone where cathodic protection fails to give satisfactory corrosion control, jackets of Monel, steel or wrought iron can be used, especially where abrasion by barges, etc., is high. These areas are shown in Figure 1.

Coatings are one of the primary means of corrosion control in the tidal area and splash zone which have severe corrosion. This paper presents the corrosive conditions prevalent on offshore platforms, the characteristics which coatings must have to combat these conditions and examples of coatings used.

Corrosive Conditions

In the tidal area and splash zone, severe corrosion occurs because of several conditions: Continuous exposure to splash and sea water spray, salt precipitation by wetting and drying action, constant exposure to moisture saturated air, moisture condensation on metal surfaces when the temperature of the metal is lower than the dew point, usually occurring from mid-afternoon on. Daily expansion and contraction of the metal where the surface is subjected to the sun (temperatures ranging from below freezing to 140 F) and maximum weathering conditions where the structure is exposed to sunlight also are corrosive conditions.

Characteristics of Effective Coatings

Any coating which is to be effective as a long-term method of corrosion control against the above conditions should have the following characteristics:

Resistance to continuous immersion in water, continuous wetting and drying and also have a low water adsorption and moisture vapor transfer rate.

Resistance to ionic transfer and act as a barrier to the penetration of chloride, sulfate, carbonate or similar ions which start under-film corrosion.

Strongly dielectric to resist the passage of any electrons which might exist from anodes set up in breaks in the coating.

Highly weather resistant because offshore structures are subject to maximum weather exposure.

High degree of chemical resistance to continuous exposure to salt, drilling muds with a wide range of pH and organic materials such as diesel and crude oils. All of these chemicals may be in contact with the coating continuously.

Strongly adherent because the tidal area and splash zones are subjected to impact damage by barges, work boats, logs, debris, etc.

Abrasion resistance to prevent being eroded away from this area.

Strong adhesion to resist film under-cutting when abraded.

Inhibitive so that the material of the coating will tend to minimize any breaks and tend to restrict corrosion even though bare metal is exposed.

Ease of application, especially in difficult areas such as welds, corners and edges.

Easy touch-up in the field. Offshore structures are subjected to considerable damage during construction; therefore

Abstract

Corrosion conditions in the tidal area and splash zone of offshore platforms are briefly discussed with the characteristics needed for a coating to be an effective means of corrosion control. Seven coatings which were inspected in service are presentd with their characteristic properties and results. Four composite coatings are also given with an evaluation of their comparative effectiveness.   2.2.5

the touch-up of coatings in the field must be easy and as effective as the original coating.

Long life and ability to maintain effective protection for many years. Drilling operations alone on multiple well platforms require several years.

Coatings Used

Many types of coatings have been used on offshore structures. Some characteristic properties and results of their use are given for seven coatings inspected in operation.

Fish Oil

Periodic applications of fish oil have been tried for protection on several structures. The advantage of simple application is offset by the necessity of re-application every few months. Even continuous re-application does not keep the structure corrosion free in the difficult areas.

Rubberized Asphalt Mastic

Though heavy, ⅛ to 3/16 inches thick semi-rubbery and adherent, rubberized asphalt mastic has provided only temporary protection. The material is relatively soft, and the abrasion in the splash zone causes rapid loss of the coating with resultant serious corrosion. In areas subjected to severe weather and sunlight, this mastic has checked

Offshore Structures —

and crazed. Areas with less than average film thickness have allowed ionic passage to the steel with corrosion starting underneath the coating. Diesel and crude oils softened the coating in the drilling area.

Gunite

In thickness from 1 to 1½ inches, Gunite proved reasonably effective when weight and abrasion were not factors. Where the Gunite was cracked by abrasion, corrosion soon started between the Gunite and the steel causing the coating to spall and lose all effectiveness.

Coat Tar Wrap

Standard pipeline technique was used in coating and wrapping the pipe structure with coat tar enamel and asbestos felt. This material is effective on underground pipe lines, but it checks, cracks and loses adhesion when subjected to marine conditions and weather.

Galvanize Plus Asphalt Emulsion

Asphalt emulsions with galvanizing have protected structures from serious corrosion. The porous asphalt emulsion provided little or no protection to the galvanizing which was incrusted heavily with white zinc carbonate—the first step toward corrosion of the underlying steel surface.

Zinc Spray

Parts of several platforms and their equipment have been coated with sprayed metallic zinc. This coating would seem to have many advantages, especially in relation to abrasion and inhibition. Because of the steel mass involved, adhesion has been a problem. Pinholing is common because of the inherent porosity of the sprayed zinc metal. High costs and the possibility of porosity under marine conditions, even though overcoated, limit the usefulness of this coating system.

Catalyzed Epoxy Coatings

Catalyzed epoxy coatings have been effective when properly applied. A tendency toward brittleness and a low resistance to extreme weather have caused some premature failure of this material.

Composite Coatings

Four composite coatings have been effective in controlling corrosion under actual operating conditions.

The first of these composites was a vinyl mastic coating consisting of a prime, two coats of a vinyl mastic and two coats of vinyl seal with a total thickness of 12 to 20 mils. This material was applied over a thoroughly clean sandblasted surface to provide a coating which meets most of the requirements for protection in marine conditions. Of all the organic coatings inspected, this system appeared to be giving best service.

Chlorinated rubber mastic, a second composite coating, consists of a wash prime, a tie coat, three coats of mastic and one or more coats of a chlorinated rubber top coat. Applied in 15 to 20-mil thicknesses, this system has most of the required properties for long service under difficult marine corrosion conditions. It may be slightly less tough than the vinyl mastic but is roughly equivalent in effectiveness.
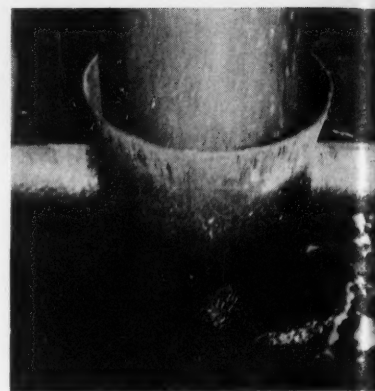
Figure 2—Inorganic silicate coating used for protection of tidal area of an offshore platform. Note the growth of moss.

Another coating outstanding in its resistance to continuous salt spray and ocean weather conditions is composed of zinc lead silicate. It has been in service on offshore structures for more than five years. Applied in 2 to 4-mil thickness over a sandblasted surface, this material is unaffected by weather and shows no change when subjected to continuous exposure of salt spray and splash conditions. Showing no tendency to chalk, check or lose adhesion, it is extremely hard with strong adhesions to steel to provide greater abrasion resistance than the softer organic products. Because of its zinc content, this inorganic coating is also inhibitive and helps protect an abraded area. An application of this coating to the tidal area of a structure is shown in Figure 2.

The offshore coating system closest to the ideal, has been a combination of the inorganic zinc silicate coating and the vinyl mastic system. This combines all the good properties of the heavy, highly resistant organic coating with the hard, abrasion resistant, highly adherent, inhibitive inorganic material. All of the last four coating systems have given outstanding service on offshore structures for several years.

Superior Coating Performance

The following steps are key factors in obtaining superior coating performance:

1. Selection of best coating for the job.

2. Strong, written specifications for the coating and its application.

3. Effective follow-up inspection.

If these three steps are followed, including effective touch-up and repair of construction damage, effective coatings with long service life can be obtained for offshore structures.

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J. I. Richardson. Corrosion in Offshore Rigs. Amercoat Corporation, South Gate, California

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The Teche Section Corrosion Control Short Course will be held in June.

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North Central Region Meeting will be held in Cleveland, October 20-22.

CORROSION ABSTRACTS

INDEX TO CORROSION ABSTRACTS

2.3.6, 6.2.5, 4.3.3, 3.5.9

An Electron Diffraction Study of Stainless Steel Corroded at High Temperature. Corrosion in Atmosphere Containing Ammonia Gas. (In English) Tadayuki Nakayama. Waseda University, Castings Research Lab. Rept. No. 8, 77-80 (1957) November.

Electron diffraction patterns of the surface layers of 13% chromium and 18-8 stainless steel corroded at 700 C by an atmosphere containing ammonia gas.—MR.   16410

2.3.7, 3.5.8, 8.9.1

Crack Propagation Tests of High-Strength Sheet Steels Using Small Specimens. J. E. Srawley and C. D. Beachem. U. S. Naval Research Lab. April, 1958, 30 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 131682).

This report describes a test for high-strength sheet materials, a prominent feature of current and projected rockets and high-speed aircraft, which may serve to provide a means of distinction between materials which could be expected to behave reliably in highly stressed structures and those which would be sensitive to minute stress raisers. The test requires only small specimens, about the size usually used for conventional tests of sheet materials, which are provided with a central transverse crack. The result is expressed as a net fracture stress, which can be compared directly with the conventional tensile strength of the material.—OTS.   16650

2.3.7, 5.4.5

Effects of Oxidation on Adhesion of Polyethylene to Metals. F. J. Bockhoff,

E. T. McDonel and J. E. Rutzler, Jr. Ind. and Eng. Chem., **50**, No. 6, 904-907 (1958) June.

Adhesion tests were made using standard buttons of Specification N: 46-5-18 stainless steel and rods of 416 stainless steel. Results showed that increase in oxidation of polyethylene increased strength of adhesion, whether polyethylene was applied to adherents as powder of film. When powder was used, fused polyethylene was exposed to the atmosphere prior to joining the adherent ends; there was much less exposure of the polymer to air when bonding was done with film, and still less when the atmosphere was nitrogen. Oxidation of film prepared from powder appeared to be appreciable, particularly at 300 C, as films showed a slight brownish discoloration. At 200 C to 225 C, however, no discoloration was observed and specimens exhibited twice the strength obtained with bonds in which the polyethylene was discolored. Mechanism of bonding is discussed. Graphs, 29 references.—INCO.   16459

2.4 Instrumentation

2.4.2, 8.4.3

Electrical Probes Monitor Corrosion. A. Dravnieks and A. J. Freedman. Standard Oil Co. Petroleum Refiner, **37**, No. 7, 107-110 (1958) July.

Discusses advantages of electrical probes, principle of the new electrical resistance method, various designs of probes and main types of application with specific reference to petroleum industry. Electrical probe offers high sensitivity for laboratory corrosion testing, and is used for monitoring existing plants, exploring new processes and solving corrosion problems in many refinery processes.—INCO.   16794

2.4.3, 4.3.5, 3.2.2

Ultrasonic Inspection Used to Detect Hydrogen Attack. J. Bland. Standard Oil Co.—Indiana. Petroleum Refiner, **37**, No. 7, 115-118 (1958) July.

Test results indicate that ultrasonic method is capable of detecting damage produced in steel by high temperature hydrogen attack. In case of sample tested, damage had resulted in cracking of reformer vessel shell, and originally was disclosed by continued cracking, in base metal adjacent to weld, during attempts to repair crack by welding. Presence of high temperature hydrogen attacks was confirmed by metallurgical examination of plugs removed from shell. Testing procedure and interpretation of ultrasonic patterns is discussed.—INCO.   16749

2.4.3, 2.3.7

Instruments Designed for Non-Destructive Measurement of Coating Thickness. C. Schuettler. Paint Ind. Mag., **73**, No. 2, 17, 50-51 (1958).

The paper deals with two devices, the Magne-Gage which measures non-magnetic coating up to 0.080 in. with a 10% accuracy and the Filmeter which measures non-metallic films on non-magnetic base metals with an accuracy of 5% up to 0.001 in. or 3% up to 0.005 in. The first device uses the principle of magnetic at-

traction against the tension of a spring. The second device uses an oscillator, coupled to a search coil, which is modulated by the eddy current set up in the base metal.—RPI.   16652

2.4.3

Automatic Electromagnetic and Ultrasonic Inspection of Steel Billets. V. Husarek. Stahl und Eisen, **77**, No. 21 1483-1487 (1957). Translation available from Henry Brutcher, Technical Translations, P. O. Box 157, Altadena, Calif.

Description of an experimental set-up for simultaneous electromagnetic and ultrasonic inspection of steel billets for a wire-rod mill: Particulars on electromagnetic unit; accessories developed for the ultrasonic (Krautkrämer) instrument. Block diagram for indication of defects classified into three groups. Routine set-up for inspection of low-carbon basic bessemer steel billets about 3 x 3 in. square section and 30 ft. length, at a rate of about 80 net tons per hr. Design details on entire automatic inspection station. Advantages: Less ingot discard; better information or billet quality; lower inspection costs; higher wire-rod mill production; better quality of the finished product. 10 figures.—HB.   16171

3. CHARACTERISTIC CORROSION PHENOMENA

3.2 Forms

3.2.2, 6.3.20

Hydrogen Embrittlement of Zirconium. R. W. Dayton, A. D. Schwope, G. T. Muehlenkamp, H. A. Saller, R. F. Dickerson, C. M. Schwartz and M. W. Mallett. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-767, Aug. 22, 1952 (Declassified March 6, 1958), 36 pp. Available from Office of Technical Services, Washington, D. C.

The amount of hydrogen normally present in zirconium and zirconium alloys suffices to reduce their ductility greatly in an impact test at room temperature, after slow cooling from 600 F. Quenching from 600 F or above gives high impact strength, as does removal of hydrogen by high-temperature vacuum annealig. The evidence on hydrogen embrittlement, the diffusion, solid solubility, equilibrium pressure of hydrogen in zirconium, the microstructure, the effects of hydrogen and heat treatment on the mechanical properties of zirconium are discussed. (auth).—NSA. 15949

3.2.2, 3.5.8, 6.2.5

Chemical Factors Affecting Stress Corrosion Cracking of 18-8 Stainless Steels. H. H. Uhlig and John Lincoln, Jr. Massachusetts Institute of Technology. J. Electrochem. Soc., 105, No. 6, 325-332 (1958) June.

Transgranular stress corrosion cracking of 18-8 Type 304 specimens in boiling 42% magnesium chloride does not depend on rate of stressing (< 1 sec to 10 min) nor on small variations in degree of plastic deformation. Cold worked specimens fail in shorter times than annealed, sheared specimens. Addition of hydrochloric acid to magnesium chloride decreases cracking time whereas addition of sodium hydroxide increases the time. Pre-exposure of unstressed specimens to magnesium chloride slightly decreases cracking times of the same specimens subsequently stressed. Cracks occur along sheared edges of unstressed specimens despite stress relief anneal at 375 C for 2 hr.

Cracks propagate along sheared edges of U-bend specimens at 0.5 to 1 cm/hr. through that portion of the specimen cross section in tension, the rate being much slower through the remaining cross section. No induction time for cracks to initiate was observed.

Sizeable pits are not necessary for cracking in magnesium chloride but appear to be essential in media like sodium chloride which in absence of pitting is not particularly active in causing cracking. The pitting mechanism produces concentrated low pH metal chlorides (e.g., ferrous chloride) within the pit, which like magnesium chloride cause immediate cracking. Oxygen is required for pitting of 18-8 as shown by Uhlig and Morrill, and hence also for stress corrosion cracking as observed by Williams and Eckel, but oxygen is not necessary in magnesium chloride or ferrous chloride.

Cracking can be prevented by cathodic protection at a current density of 0.03 ma/cm² or higher. Anodic current density up to 0.01 ma/cm² were found to have no effect on cracking tendency, nor did coupling of 18-8 to platinum. 16085

3.2.2, 5.8.2, 6.2.2, 7.2

Corrosion and Tuberculation of Cast Iron. THURSTON E. LARSON AND R. V. SKOLD. *Am. Water Works Assoc. J.,* 49, 1294-1302 (1957) October.

Calcium in the presence of alkalinity, regardless of pH or saturation index, is an effective inhibitor to corrosion in water pipes. The problem of designing water treatment to avoid tuberculation is limited to such waters as already contain inhibitors in insufficient concentrations to provide complete protection. A rate of flow sufficient to transport the inhibitor to the point of effectiveness is also necessary.—BTR. 15342

3.2.2, 7.3, 5.2.2, 6.2.2

The Nature of Pitting Attack on Cast Iron Propellers and Preliminary Experiments on Its Prevention by Cathodic Protection. Research Report No. 476. R. I. HIGGINS. *British Cast Iron Res. Assoc., J. Research and Development,* 7, No. 3, 129-143 (1957) December.

Although general corrosion attack on cast iron marine propellers is slow, some propellers are susceptible to rapid local pitting attack particularly at outer parts of blades. Incidence, form and distribution of this attack appear to be dependent to some extent on tip speed of propeller. Results of examinations of used propellers are discussed. Possible causes of pitting attack are considered. Evidence is presented to show that metal is removed by corrosion process rather than by mechanical attack by cavitation erosion. In service tests on a trawler, results showed that nodular cast iron and flake graphite iron propellers pitted in exactly the same place and to same degree. Laboratory tests with jet impact machine show superiority of nodular iron over flake graphite iron. Lack of correlation between service and jet tests infers that pitting is caused by corrosion process. Prevention of pitting attack by cathodic protection is discussed. Experiments are described in which sacrificial magnesium anodes were fitted to propellers and to hull of tugs and work boats in service and significance of contact resistance between propeller shaft and hull is reviewed. Further development work on design and construction of magnesium anode attached to propeller rather than hull is suggested. Numerous photographs, diagrams. Photomicrograph shows phosphide sweat inclusion exposed by pitting attack.—INCO. 15301

3.2.3, 6.3.11, 4.3.5

Room Temperature Tarnishing of Silver in Bromide and Iodine. Joseph L. Weininger. General Electric Co. J. Electrochem. Soc., 105, No. 10, 577-581 (1958).

Pure silver was tarnished in an atmosphere of iodine and bromine vapor at room temperature. This resulted in impervious halide surface layers, from which tarnishing rates could be deduced by means of a photomicrographic technique. It was found that the parabolic rate law, with diffusion being the rate-determining step, also holds at room temperature. The presence of water vapor reduces the rate of halogenation by a factor of two. 16700

3.2.3, 3.7.3, 6.3.6

Changes of Structure and Manufacturing Defects Caused by Scaling, in Hot Rolled Bronze. Z. Hegedus. Acta Technica, 19, No. 3-4, 363-369 (1958). (In Hungarian.)

Surface cracks formed at the first passes of hot rolling are connected with de-tinning of the surface and formation of tannic oxide in the atmosphere of the oxidizing furnace. Formation of scale proceeds in two steps. First, the tin content of the alpha-crystal oxidizes into tannic oxide and only after complete detining, the copper oxidizes. Thickness of the detinned layer is a function of the homogenization temperature and the time. 5 references.—MR. 16404

3.2.3, 2,3,9, 6.2.2

X-Ray Fine Structure Investigation on Scale Covers of an Iron-Aluminum Sinter Metal. (In German.) Franz M. Oberhauser. Z. Metallkunde, 49, 343-345 (1958) June.

Scale covers on iron-aluminum sinter metal (12 to 14% aluminum) were investigated by x rays. At 1350 granular scale covers of α-ferric oxides are formed. At 1200 the scale cover consists of a fine granular ferrous ferric oxide intermediate layer and an outer layer of α-ferric oxide and ferrous ferric oxide. For explanation it is assumed that each grain oxidizes separately. The predominance of certain stages of oxidation in the scale covers follows from the strong temperature dependence of the rates of diffusion and reaction. (auth) —NSA. 16626

3.2.3, 2.3.6, 6.2.4

Some Preliminary Results of an Electron Microscope Study of the Oxidation of Steels. A. M. Edwards and F. B. Pickering. J. Iron and Steel Inst., 189, Pt. 1, 55-57 (1958) May.

Investigation of oxidation effects on low alloy steels of the type used in power plants. In steels examined, oxidation followed same general sequences. At short times, a number of whisker growths of oxide were observed and as time of oxidation increased the number and length of whiskers increased. With further periods of oxidation, thin blades of oxides began to form while the number of whiskers decreased and eventually these blades began to impinge at their bases to form compact layers of oxide. Still further oxidation resulted in blades developing crystallographic surfaces to become very thin prisms. Marked thinness of blades and prisms, as shown by their transparency to electron beams, resulted in electron diffraction patterns being observed, which indicated that oxides were ferric oxide. As temperature of oxidation increased, various stages of growth of oxides occurred at shorter times, and in the early stages of whisker growth it was observed that lengths of whiskers on various steels examined placed oxidation resistance of these steels in the same order as conventional scaling tests. Photomicrographs.—INCO. 16035

3.5 Physical and Mechanical Effects

3.5.3, 6.3.11, 3.6.6

Physical Processes in Contact Erosion. L. H. Germer. Bell Telephone Labs. J. Applied Phys., 29, No. 7, 1067-1082 (1958) July.

Various causes of erosion of noble metal contacts have been isolated. They give adequate interpretation of sign of erosion under various circuit conditions, and of space distribution of eroded metal, as well as quantitative agreement with measurements of erosion in repetitive tests. Electric arcs are chief cause of

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erosion, although at breaking contacts glow discharges may be important, and at higher currents bridge erosion is significant also. Anode arcs (which corrode anode) occur at small contact separations, and cathode arcs (which erode cathode) appear at large separations. Metals studied were palladium and silver. Erosion of these metals in inactive condition is of order of 4×10^{-14} cc/erg in anode arcs and less than this by small factor in cathode arcs, or break as well as on closure. In glow discharge only chemically active metal silver is appreciably eroded. Activation produced by organic vapors often changes magnitude of erosion per unit of arc energy. Graphs, photomicrographs.—INCO.   16503

3.5.4, 8.4.5
Radiation Effects in Magnetic Materials. D. I. Gordon, R. S. Sery and R. E. Fischell. U. S. Naval Ordnance Lab. Nucleonics, **16**, No. 6, 73-77 (1958) June.

Magnetic-property changes induced by reactor radiation were measured in Orthonol, 5-79 Mo Permalloy, 2 V Permendur, 16 Alfenol, nickel ferrite and 2-81 Mo Permalloy. 5-79 Mo Permalloy and Orthonol show the most significant changes; 16 Alfenol and 2 V Permendur, the smallest. Between these two extreme groups lie nickel ferrite and powdered 2-81 Mo Permalloy, which show small changes in permeability but substantial changes in the frequency core-less characteristics in the frequency range of 10-50 kcps. None of the 3 cores tested for magneto striction changes showed appreciable effect. Permanency of effects is shown by constancy of peak induction for several materials as a function of time after end of irradiation period. Additional measurements of d-c and a-c properties at later dates continue to indicate that changes in properties induced by irradiation are permanent. Graphs, tables, 22 references. —INCO.   16723

3.5.4, 4.4.10, 8.4.5
Dynamic Corrosion in Polyphenyls Under Irradiation. H. E. Kline, N. J. Gioseffi and W. N. Bley. Atomic International Div., North American Aviation, Inc. U. S. Atomic Energy Commission Pubn., NAA-SR-2046, May 15, 1958, 29 pp. Available from Office of Technical Services, Washington, D. C.

Corrosion specimens of various materials were exposed to polyphenyls in the NAA-20 loops at MTR, and compared with out-of-pile specimens in the same coolant streams over the temperature range of 500 to 650 F. Aluminum, 304 and 410 stainless steel, carbon steel and 4130 alloy steel exhibited good to excellent resistance. Magnesium and zirconium were unsatisfactory. Integrated neutron fluxes of the order of 2×10^{19} thermal and 10^{18} fast, did not affect the corrosion resistance of the materials studied. (auth). —NSA.   16565

3.5.4, 6.3.11, 6.3.20, 4.3.2
Effect of α-Activity on the Corrosion Rates of Platinum and Zirconium in Hydrobromic Acid. (In Russian.) D. M. Ziv and I. A. Efros. Atomnaya Energiya, **4**, No. 3, 293-294 (1958) March.

The corrosion rates of 99.9% pure platinum and zirconium foils in hydrobromic acid in the presence of Po^{210} with an α emissivity of 0.3 to 1 mc were determined. At room temperature the presence of α activity did not affect the corrosion rate of platinum foil; at 80 C a slight increase in corrosion rate was observed. The completely submerged specimens corroded faster than the partially submerged ones.

The presence of polonium in quantities of 0.25 to 0.3 mc increased the corrosion rate of zirconium approximately 100 times. —NSA.   16679

3.5.4, 3.5.9, 3.8.4
Measurements of Total Hemispherical Emissivity of Various Oxidized Metals at High Temperature. William R. Wade. Langley Aeronautical Lab. U. S. National Advisory Cttee. for Aeronautics, Technical Note No. 4206, March, 1958, 44 pp.

The results of measurements of total hemispherical emissivity over the temperature range of 600 to 2,000 F for various heavily oxidized metals are presented, together with a description of the equipment and the procedures used. The variation of total emissivity due to oxidation of the materials is presented, up to the highest temperature which produces an adherent oxide coating. Results from investigations to determine any deviation of the thermal radiation from Lambert's cosine law for the oxidized metals are presented. (auth) —NSA.   16678

3.5.4, 8.4.5, 3.4.3
Radiochemical Analysis of Crud from the Army Package Power Reactor. J. L. Zegger, W. J. Small and W. S. Brown. Alco Products Inc. U. S. Atomic Energy Commission Pubn., APAE-26, Feb. 15, 1958, 34 pp. Available from Office of Technical Services, Washington, D. C.

A study was made of the radiochemical composition and the specific activity of insoluble corrosion products (crud) removed from the primary system of the APPR-1. The results of analysis of twelve crud samples collected during the interval from September 3, 1957 to December 1, 1957 are presented. The samples were radiochemically analyzed for long-lived gamma emitting nuclides only. Data are presented on the measured values of the specific activity of crud, the ratios of the nuclide specific activities, and the concentration of crud (crud level) in the circulating primary water. Also included are data, based on the analysis of a single sample, comparing the specific activity of the deposited and circulating corrosion products. (auth)— NSA.   16685

3.5.8
Mechanism of Intercrystalline Fracture. H. C. Chang and N. J. Grant. Paper before Am. Inst. Mining Met. Engrs., New York, February, 1956. *J. Metals* (Trans. AIME), **8**, No. 5, 544-551 (1956) May.

Microscopic observations, made during creep tests, of initiation and propagation of intercrystalline fractures of aluminum-20 zinc, 80 nickel-20 chromium, 2S and 3S aluminum alloys, with particular attention to cracks in aluminum-20 zinc coarse-grain specimens with known geometry of grains and grain boundaries. Intercrystalline cracking occurs when deformation accommodation in grains is not realized. Boundary sliding gives rise to 3-dimensional stresses at triple point. Largest tensile stress normal to grain boundary surface may exceed cohesive stress of grain boundary. Propagation of cracks along nearly horizontal boundary is promoted by normal stress acting across boundary and propagation along inclined grain boundary is result of shear stress along boundary. Rate of propagation of intercrystalline cracks depends on ability of grains to deform. In 80 nickel-20 chromium alloy, granular deformation was small and rate of cracking high; while in aluminum-zinc alloy with higher total ductility, in-

tercrystalline crack propagation was slower. Diagrams, photomicrographs, 18 references.—INCO.   12397

3.5.8, 6.2.5, 4.3.6
The Stress-Corrosion Cracking of Austenitic Stainless Steels. Part I. Mechanism of the Process in Hot Magnesium Chloride Solutions. T. P. Hoar and J. G. Hines. *J. Iron Steel Inst.*, **182**, 124-143 (1956) Feb.

Several types of stainless steel wires based on 18% chromium. 8% nickel, stressed in tension, were exposed to 42% aqueous magnesium chloride solution at 135 to 154 C. Corrosion potential and extension were measured. Diagrams, micrographs, tables, graphs. 33 references.— MR.   12440

3.5.8, 6.2.5, 6.4.2
Onset of Fast Crack Propagation in High Strength Steel and Aluminum Alloys. G. R. Irwin. Naval Research Laboratory, May, 1956, 16 pp. Available from: Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order

3.5.8, 6.2.5, 6.4.2
Force tendency, a concept of driving force per unit crack front, was applied to fracturing in metals. Measured values of the crack extension force at the onset of fast fracturing for a variety of materials are shown. Practical use of critical values of crack extension force is illustrated.   12509
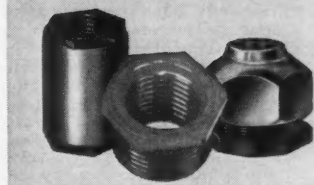
3.5.8, 3.7.1
On the Problem of Intercrystalline Corrosion and Stress Corrosion of Homogeneous Copper-Gold and Copper-Zinc and of Precipitable Aluminum-Zinc-Magnesium Mixed Crystals. (In Ger-

man.) H. KLATTE. *Werkstoffe u. Korrosion,* **7,** Nos. 10, 12, 545-560, 708-716 (1956) Oct., Dec.

Mixed crystals of homogeneous gold-copper (10-90 gold) and of copper-zinc (63-80 copper) were subjected to tensile stress under mercury at room temperature in order to investigate conditions under which stress corrosion of homogeneous mixed crystals occurs and to establish a theory for formation of cracks. Tensile strength decreases greatly, amount depending on concentration of mixed crystals, with maximum at 50% atomic weight. Same effect may be produced by chemical agents, but effect is limited to the less noble side of the mixed crystal system. Results with ferric chloride and ammonia are presented. Since decrease of tensile strength does not occur with pure metals, it is suspected that the grain-boundaries of mixed crystal systems have increased reactivity producing susceptibility to stress corrosion. Stress corrosion cracks are explained by fact that corrosive agent reacts more intensely upon deformed materials as their reactivity under deformation is much higher. Corrosion tests under constant tensile strength of an aluminum-zinc-magnesium alloy in 3% aqueous sodium chloride solution with 0.1% hydrogen peroxide are described. Effect of addition of chromium and influece of heat treatments, homogenizing temperatures, retarded chilling and storage at room temperature between homogenizing and tempering upon sensitivity to corrosion under tensile stress were investigated. Numerous graphs.—INCO.   13214

3.6 Electrochemical Effects

3.6.2, 6.4.2
The Corrosion Mechanism of Metals in Narrow Fissures and Crevices. Pt. IV. Corrosion of Aluminum and Its Alloys. (In Russian.) I. L. Rozenfel'd and I. K. Marshakov. J. Phys. Chem., USSR (Zhur. Fiz. Khim.), **31,** 2328-2335 (1957); Chem. Abstracts, **52,** No. 10, 8011 (1958) May 25.

The corrosion of aluminum and Alclad alloys in sodium chloride solutions was studied. The metal-corrosion rate in narrow fissures was higher by about one order of magnitude than that of metal in free contact with the solution, owing to the formation of micro voltaic cells with the metal under different conditions with an unequal supply of oxygen in the two conditions. The differential oxidation was the original cause of formation of the micro voltaic cells, but the effects of the micro voltaic cells were influenced by changes in the pH of the solutions in immediate contact with the metal during anodic polarization. The negative difference effects upon the aluminum surface in the narrow fissure reached 40-47%. The exceptional differential effect was caused by the solution in the fissure becoming acid through the hydrolysis of the products of anodic reactions.—ALL. 16325

3.6.3
The Corrosion of Metals with Imperfect Coatings. (In German.) HANS-JÜRGEN ENGELL. *Archiv. Eisenhuttenw.,* **28,** No. 11, 753-760 (1957) Nov.

Shows how the electric resistivity of solution and coating affects corrosion. Some methods for measuring the electrochemical reactions during corrosion of metals with imperfect coatings are reported.—BTR. 15240

3.6.5, 5.4.5
Note on the Characteristics of Potential/Time Curves for Painted Non-Ferrous Metals. J. H. Greenblatt. J. Applied Chem., **8,** Pt. 4, 299-232 (1958) April.

The potentials of steel, aluminum, brass and copper rods overcoated with various paints were measured in sea water over a period of time. The potentials obtained in all cases were determined by the substrate metal rather than the paint coating used. The potential/time curves on copper, brass and aluminum have the same characteristics as those on steel. 5 references.—RPI. 16516

3.6.5
Metal Electrode Potentials in Pure Water. W. Tomassi and A. Houwal. (In Polish.) Przemysl Chem., **13,** 82-87 (1957); Chem. Absts., **51,** 12703 (1957).

The potentials of mercury and platinum electrodes in water were determined. Measurements were made in water with specific conductance in the range $10^{-8} - 3.5 \times 10^{-6}/\Omega$ cm, with and without air. Platinum plates covered with platinum black in different degrees of dispersion, and platinum wire, both smooth and covered with platinum black, were used. Hydroxyl ion concentration, purity of water and the degree of dispersion of the electrode surface were found to influence the value of the potential obtained.—M. 16370

3.6.6
Study on Galvanic Corrosion of Metals. (In Japanese.) Hiroshi Asada and Shiro Kohara. Light Metals (Japan), No. 31, 35.39 (1958) July.

Corrosion tests of copper, iron, zinc and aluminum in 5.85% sodium chloride solution containing 0.3% hydrogen peroxide were carried out for each metal by itself in the solution, for galvanic couples formed by two of those metals, and for contacts of the following three metals, copper-iron-zinc and copper-iron-aluminum. In the case of uncoupled metals, zinc was corroded most severely and iron was next. Copper and aluminum were less corroded. For galvanic couples, however, basic metal in a couple was corroded perferentially as predicted from the Galvanic Series chart. In the case of contact of three metals, only the most basic metal was corroded, while the other two metals were protected from corrosion. Protection by loss of anodic metal decreased with time i.e. with a decrease in corrosion current; when the corrosion current reached zero, each metal corroded independently. It was concluded that decrease in corrosion current resulted from thickening of the hydrate film formed on the surface of the metal. (auth.)—ALL. 16757

3.6.6, 8.1.2
The Corrosion of Buildings. Pt. II. The Juxtaposition of Incompatible Materials. J. R. D. Heming. Corrosion Prevention and Control, **5,** No. 6, 85-86 (1958) June.

Deals with building materials which should not be used near or in contact with each other. Cement, concrete and similar substances, when cured and dry, have no effect on non-ferrous metals but when 'green' tends to cause corrosion. Copper and zinc should be insulated from each other if used in the same assembly, and drainage water from copper surfaces should not be allowed to fall on zinc or galvanized steel.—ZDA. 16510

3.6.6, 6.2.5
The Corrosion of Stainless Steels at the Points of Contact with Nonmetallic Materials. I. B. Ulanovskii and Yu. M.

Korovin. (In Russian.) J. Applied Chem., USSR (Zhur. Priklad. Khim.), **31,** No. 9, 1366-1370 (1958). Translation Available from Associated Technical Services. P. O. Box 271, East Orange, N. J.

One fundamental reason for corrosion at these points of contact is found to be activation of the metal surface because of a reduction in the pH of the electrolyte, leading to continuous functioning of the galvanic couple: contact-surrounding medium. 8 figures, 9 references.—ATS. 16682

3.6.8, 3.6.5, 6.3.3
Cathodic Polarization of Active Chromium-Iron Alloy in Sulphuric Acid. (In German.) Th. Heumann and B. Röschenbleck. Werkstoffe u. Korrosion, **9,** 389-390 (1958) June.

Cathodic polarization curves and rest potentials were measured with respect to pH of the electrolyte. Behavior of rest potential deviates from that of the hydrogen electrode. In the range of pH values investigated, cathodic polarization curves of the deposition of hydrogen are parallel. Exchange currents rise with increasing acid concentration and increasing chromium in the alloy. 15 references. —MR. 16508

3.6.8, 3.2.2, 6.2.5
Effect of Cathodic and Anodic Polarization on the Rate of Corrosion Cracking in Stainless Steel. (In Russian.) V. V. Romanov and V. V. Dobrolyubov. Metalloved. i Obrabotka Metallov, No. 7, 19-21 (1958) July. Translation Available from Henry Brutcher, Technical Translations, P. O. Box 157, Altadena, California.

Cathodic polarization retards and can fully stop corrosion cracking. Anodic polarization, on the other hand, speeds the process. Polarization has an effect on the character of corrosion cracks, on their shape and form of development. Increase in temperature raises the strength of the protective cathodic current while the acceleration of the influence of anodic polarization was attained under much lower temperatures. 7 references.—MR. 16730

3.7 Metallurgical Effects

3.7.2, 3.2.3, 6.2.2, 3.5.9
The Influence of Silicon Content on the Growth and Scaling Resistance of Cast Iron with Nodular Graphite. R. J. Maitland and I. C. H. Hughes. British Cast Iron Research Association. J. Research and Development, **7,** No. 5, 203-223 (1958) April.

Growth and scaling behavior of nodular irons with 1.2 to 5.7% silicon at temperatures within the range of 650 to 1000 C. Both growth and scaling proceed relatively slowly and are inhibited by increasing silicon contents at temperatures below the austenite transformation range. When the critical temperature range is exceeded or nearly exceeded, growth and scaling become excessive and seem to be promoted by silicon. 21 references, 19 plates.—MR. 16107

3.7.2, 6.3.15, 6.3.20
Alloys of Titanium and Zirconium Containing Tin. R. F. Smart. Tin Research Inst. Metallurgia, **57,** 181-188 (1958) April.

Tin is an important alloying element in titanium and zirconium, especially in those alloys designed for creep and corrosion resistance. A review is presented

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of the effect of tin on titanium and zirconium and of the properties of alloys of those metals containing tin. (auth) —NSA. 16064

3.7.2
Distribution of Alloying Elements Between Solid and Liquid Phases in Alloys. B. A. Movchan. Bull. Acad. Sci. USSR, Tech. Sci. Section (Izvestiya Akad. Nauk SSSR, Otd. Tekh. Nauk), No. 4, 122-123 (1958) April. (In Russian.) Translation available from Henry Brutcher, P. O. Box 157, Altadena, Calif.

Microradiographic study of distribution of silver, copper and zinc between solid and liquid phases in binary aluminum alloys . . . segregation films at solid/liquid interface. 4 figures.—HB. 16556

3.7.2, 6.3.17, 3.4.9
The Effects of Ternary Alloying Additions on the Corrosion Resistance of Epsilon-Phase Uranium-Zirconium Alloys. James E. Reynolds, Warren E. Berry, Harance R. Ogden, Robert S. Peoples and Robert I. Jaffee. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-1087, April 27, 1956 (Declassified March 22, 1957), 36 pp. Available from Office of Technical Services, Washington, D. C.

The corrosion rate in 680 F water of the uranium-50 wt% zirconium binary alloy was found to be —0.20 mg/(cm²)(hr), and that of the uranium-40 wt% zirconium binary alloy was —0.34 mg/-(cm²)(hr). Both alloys corroded uniformly, with no evidence of discontinuous failure. Normal variations in interstitial content in either alloy had no significant effect on corrosion behavior. Tantalum additions, in the range of 0.2 to 5 wt%, improved the corrosion rate of the uranium —50 wt% zirconium, with a minimum rate of —0.06 mg/(cm²)(hr) for the 5 wt% tantalum alloy. The 5 wt% tantalum addition to the uranium —40 wt% zirconium alloy decreased the corrosion rate of the base condition only. In other conditions, the 5 wt% alloy failed discontinuously. All other additions to both bases either had no effect or decreased corrosion resistance. These included aluminum, chromium, iron molybdenum, nickel, platinum, tin, titanium, tungsten and vanadium additions. (auth).—NSA. 16405

3.7.2, 6.3.17, 3.5.4
Observations on the Effect of Carbon in Uranium Subject to Thermal Cycling and Pile Irradiation. W. E. Seymour and J. F. Duffey. Knolls Atomic Power Lab. U. S. Atomic Energy Commission Pubn., KAPL-1102, July 14, 1954 (Declassified Feb. 26, 1957), 31 pp. Available from Office of Technical Services, Washington, D. C.

Carbon in amounts of 0.2 wt.% and over has been observed to improve the dimensional stability of uranium subject to thermal cycling. It has also been observed to increase the corrosion resistance of uranium in boiling water and to result in a finer alpha grain size after recrystallization. Carbon does not seem to improve the dimensional stability of uranium exposed to a neutron flux, although high alpha recrystallization of cold-worked uranium improves the dimensional stability by a ratio of 5 to 1 upon pile irradiation. (auth)—NSA. 16339

3.7.3, 8.2.2
Ferritic-Austenitic Weld Joints in Thermal Power Stations. F. Zimmer. Rev. Met., **3**, No. 4, 162-174 (1957) Oct.; Engrs' Digest, **19**, No. 3, 99-102 (1958) March.

To prevent problems associated with

weld joints between ferritic and austenitic steels, particularly effects of thermal and pressure cycling, specially alloyed and stabilized steels are employed, and special joints developed. Survey is given of principal types of ferritic-austenitic weld joints used at present time, includ-

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South Central Region Meeting has been set for October 12-15 in Denver.

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The Teche Section Corrosion Control Short Course will be held in June.

ing an assessment of extent to which they succeed in preventing problems of mechanical stresses, carbon mitigation and stress corrosion in decarburized zone. Review covers: electrically heated joints; joints using stabilized ferritic steel (stabilized with titanium or niobium); ferritic-austenitic joints with protective overlay (80 nickel-20 chromium); joints with special nickel-chromium weld metal containing niobium and tantalum (Babcock & Wilcox 50 nickel/10 chromium weld metal, also Inco Rod A); transition joints with intermediate coefficients of expansion (80 nickel-3 chromium-0.8 niobium-0.07 carbon) by Sandvik, alloy containing 30-40 nickel and 10-15 chromium by Firth-Brown; Kelcaloy transition joints (Kellog Co. joint comprising internal forged ferritic tube with austenitic steel cast into it); British Babcock & Wilcox joint (inner austenitic tube cold-expanded into outer ferritic tube); Mannesmann transition joint (ferritic outer element and austenitic inner element interfaced with electrolytically deposited nickel); flanged joints; mechanical interlocking of ferritic and austenitic members with 2 ferritic-austenitic seal-welds between them (used at Leverkusen Power Station in Germany); and sintered-metal joints. Diagrams illustrate the joints under consideration.—INCO.
16361

3.7.3, 6.2.5

Cooperative Investigation of a New Welding Electrode for Stainless Steel. R. D. Wylie. Paper before American Soc. Mechanical Engrs.-American Welding Soc. Joint Metals Eng. Conference, St. Louis, April 15-17, 1958. ASME Paper No. 58-MET-6, 1958, 8 pp.

Extensive tensile tests were made on 16-8-2 weld metal in the as-welded condition and after various postweld thermal treatments, including long-time aging at elevated temperatures. Results indicate that postweld solution-treatment decreases tensile and yield strength of deposited weld metal with a concomitant increase in elongation and reduction of area. Aging at elevated temperatures has a similar effect on as-welded tensile properties without increasing ductility. There was a slight increase in yield strength of solution heat-treated weld metal after aging, however, the ductility remained in the range for unaged properties. In order to qualify a welded joint properly for ASME Code construction a full-size joint must be welded and subjected to a series of mechanical tests. These tests include transverse tensile tests and bends. Since this welding procedure was qualified for Type 347 and 316 base materials in tube, pipe and plate form, a number of such tests were made. Results of these tests are given. Graphs, 16 references. (auth)—INCO.   16681

3.7.3

Electrode-Tip Life Studies in Series Spot Welding. E. F. Nippes, W. F. Savage, S. M. Robelotto and K. E. Dorschu. Paper before Am. Welding Soc., National Spring Mtg., Philadelphia, April 8-12, 1957. Welding J., **37**, No. 6, 241s-248s (1958) June.

Effects of electrode geometry, electrode material, electrode force and welding current on weld strength, weld diameter, weld consistency and electrode life were investigated for series spot welds in as-received auto-body stock. Material was cold-rolled, rimmed steel supplied in pickled-and lightly

oiled condition; analysis shows 0.05 nickel content. As result of study, optimum combination of welding variables was determined. Study of effect of electrode geometry on weld consistency indicated that 2-in. continuous-radius domed electrode provided more consistent welds than 5/16-in. continuous-radium dome often used in commercial practice. Additional study showed that welding conditions which did not produce flashing at electrodes provided more consistent welds than conditions which caused flashing. Tables, graphs, diagrams.—INCO.   16613

3.7.3, 8.4.3, 3.4.8, 5.3.2

New Concept Solves Aluminized Pipe Weld Problems. Kenneth R. Notvest. Petroleum Refiner, **37**, No. 7, 100-102 (1958) July.

Aluminum coated materials have found wide acceptance in oil refineries as a cure for hydrogen sulfide scaling. However considerable difficulty has been encountered in welding these materials. By controlling the fusion of the aluminized base metal with the filler metal to give an alloyed root pass, this alloy root pass is fused to the base metal coating thereby providing continuous aluminum protection from corrosion. Inert gas welding with controlled heat input, filler metal and travel speed provides a root pass with 3% average aluminum content. The inside surface of the root pass will run 8 to 10% aluminum with no peeled back coatings or unprotected areas. The remainder of the weld is finished in conventional fashion. The root pass is inert gas welded with controlled heat input and the addition of filler rod. The coating goes into solution in the weld fusion zone, alloying the root pass with 2 to 6% aluminum. As the bead freezes, the still molten coating tends to flow over the root, bringing the aluminum content up considerably, at the surface. The normal coating is bonded to the weld providing a continuous protection across the weld. Results of oxidation tests at 1100 F for 100 hrs showed the surface of the weld discolored but there was no measurable scaling. Weld sections did not reveal any evidence of the presence of oxidation or nitrides in the aluminum alloy structures.—ALL.
16619

3.7.3, 5.9.4, 1.2.2

The Production Man's Guide to Adhesive Bonding Methods. J. P. Wright. Am. Machinist, **102**, No. 13, 85-92 (1958) June 30.

Faster output, lower labor and material costs are 3 prime reasons why adhesive bonding is replacing welding, brazing, soldering and mechanical fastening in wide variety of metal working applications. Review covers factors to be considered in selecting an adhesive, preparation of surface, preparation of adhesive, coating adhesive on parts, assembling parts, and allowing bond to develop. Advantages of adhesive bonding are enumerated. Chart shows comparative characteristics of typical metal-bonding adhesives. Ready-to-use, no-mix, epoxy adhesive costing about $2 per lb. has replaced silver solder ($18 per lb.) in assembling of Alnico magnets.—INCO   16675

3.7.3

Joining of Metals in Solid State by Ultrasonic Vibrations. (In Russian.) Yu. I. Kitaigorodskii et al. Bull. Acad. Sci., USSR, Tech. Sci. Section (Izvestiya Akad. Nauk SSSR, Otd. Tekh.

Nauk.), No. 8, 88-90 (1958) Aug. Translation available from Henry Brutcher, Technical Translations, P. O. Box 157, Altadena, California.

Quality of spot and continuous joints obtained with the use of ultrasonic waves as function of physical properties, surface condition, and thickness of metals joined, on the other hand, and the operating conditions of the ultrasonic apparatus, treating time, contact force, and contact surface, on the other. Materials used in study: copper, aluminum, duralumin and stainless steel sheets. Data on power consumption, vibration, frequency and amplitude, mechanical strength of joints, best treating time, etc. Microexamination of deformed-metal structure of joints. Applicability of process to a wide variety of metals and alloys. 3 figures.—HB.   16569

3.7.3

The Improvement of Welded Structures by Subsequent Forging Operations. W. R. Wollering and E. H. Lundby. Paper before Soc. of Automotive Engrs., Summer Mtg., Atlantic City, June 5, 1957. Trans. SAE, **66**, 261-266 (1958).

Description of a new technique of utilizing the subsequent forging of welded structures. Method results in development of physical properties in welded sections of alloy materials including 4340 steel and 440 A stainless steel, approaching those of the wrought parent material. Advantages of process include weight reduction in dynamically stressed wrought-steel assemblies, increase in design factor values and conservation of critical alloy materials. Photomicrographs, tables. (auth)—INCO.
16672

3.7.3

Automatic Remote Welding. (In Russian.) N. T. Shvetskov and B. Kh. Voskan'yan. Avtomat. Svarka, No. 5, (62), 62-71 (1958).

The method and machine described make possible automatic remote-controlled welding in inaccessible spots. The first uses will be in repair of weld joints on pipelines in closed trenches or in highly corrosive media. The machine has a pneumatic membrane defectoscope, a milling head, a welding head, and a blower for air or shielding gas mounted in one common housing which will be sunk into a trench to the pipe when the machine is installed on the manhole. The work of all mechanisms in the workhead housing can be watched by a mirror which is movable and can be turned into any position around a pipe. The design and operation of the equipment are described in detail and technological recommendations are given.—NSA.   16637

3.7.3., 6.2.4, 6.2.5

Steel for Welded Structures and Pressure Vessels. G. P. Smedley. Paper before Journées d'Automne, 1957. Rev. Met., **55**, 323-332 (1958) April.

Review of history of fusion welding for manufacture and repair of structures and pressure vessels, stressing importance of adequate notch toughness of welded steel sheets. Requirements of routine test for checking notch toughness are given. Discussion is included of several steels suitable for structural and pressure-vessel welding, including those containing 3.5 or 5% nickel, low-alloy nickel-chromium-copper and nickel-chromium-molybdenum-copper (U.S.S. T1) steels, and 18/8

stainless steels. Use of such steels is examined in relation to service stressing, operating temperature, type of construction and residual stress.—INCO.

16634

3.7.3

General Considerations in the Welding of Materials for Industrial and Chemical Plant. M. Birkhead. Paper before Inst. Welding, Spring Mtg., Harogate, May 10, 1958. Brit. Welding J., **5**, No. 5, 202-211 (1958) May.

Deals in general terms with welding processes, techniques and problems associated with manufacture of industrial and chemical plant in mild steel, stainless steel, stainless-clad, nickel and nickel alloys and aluminum and its alloys. Reference is made to specific cases of tank and vessel fabrication. Welding details are given for road tanker made from welding-grade A-T nickel for bulk transport of pure phenol. Photographs.—INCO. 16439

3.7.3

Spraywelding—A Hard Facing Preventive Maintenance Process. J. R. Smith. Bethlehem Steel Co. Paper before Am. Iron & Steel Inst. Iron & Steel Engr., **34**, No. 9, 90-94; disc. 94-95 (1957) Sept.

Basic operations of spraywelding process—preparation of surface, spraying the surface and fusing overlay—are described. Finishing the fused overlay may be most satisfactorily accomplished by grinding; machining with carbide tools will also produce good results. Properties of #4, #5 and #6 Sprayweld overlays (nickel-chromium-boron) are listed, as are base metals which can be spraywelded. Graphs show red hardness curves for #4, #5 and #6 alloys, and comparative corrosion resistance of alloy #6 and 18-8 in sodium hydroxide, sulfuric acid, nitric acid and glacial acetic acid. Applications mentioned are related to steel plant maintenance: table roller and shafting journal sleeves, split journal sleeves, gas engine valves, hot blast valve seats for blast furnace stoves, pins and swing grinder pulleys, packing gland bolts, cast iron steam valves and induced draft fan impellers. In discussion, question of nickel-iron castings vs spraywelded gray iron castings was brought up; while the former is less expensive, it would not have the corrosion or wear resistance of the latter. —INCO. 16283

3.7.4, 5.3.4

The Relationship Between the Structure and Properties of Nickel Electrodeposits. (In Russian.) G. S. Vozdvizhenskii and R. S. Saifullin. J. Phys. Chem., USSR (Zhur. Fiz. Khim.), **32**, 831-833 (1958) April.

X-ray study revealed no direct relation between preferential orientation of crystallites in nickel-deposits along (001) axis and their properties. This is attributed to masking effect of grain structure. It is recommended that relation between texture and deposit properties be studied under conditions ensuring identical grain structure.—INCO. 16692

3.7.4, 3.7.3, 6.3.10

Study of Structural Changes in Nickel-Chromium Alloy During Creep. (In Russian.) G. Ya Kozyrskii et al. Bull. Acad. Sci., USSR, Tech. Sci. Section (Izvestiya Akad. Nauk SSSR, Otdel. Tekh. Nauk), No. 8, 90-92 (1958) August. Translation available from:

Henry Brutcher, Technical Translations, P. O. Box 157, Altadena, California.

X-ray study and micrographic analysis of an 80.2% nickel, 19.8% chromium alloy for changes in structure during creep. Preparation of two series of specimens for creep testing, annealed at different temperatures and pressures and for different times, and of a third series without any preliminary heat treating. Data on total strain, creep rates during the different stages of creep and hardness as function of initial structure. X-ray photographs and their evaluation in conjunction with microexamination of specimens. Possibility of lengthening the service life of alloys by selecting an initial structural state that will give a minimum creep rate in the second stage of creep. 4 figures. —HB. 16695

3.7.4, 3.7.3

The Niobium-Hydrogen System. C. Wainwright. National Physical Lab., Teddington, Middlesex. J. Inst. Metals, **86**, 68-69 (1958) July.

A number of X-ray photographs were obtained from heavily cold-worked samples, and these show the short intense arcs which are typical of highly orientated material. It is found that when sufficient hydrogen is introduced into such samples to show hydride lines, the additional lines reproduce the orientations of the matrix. This relationship is in accordance with Brauer's analysis, and with the development of the hydride phase by deformation of the niobium lattice, rather than by the nucleation and growth of independent crystals. It also suggests that highly worked samples may serve more generally to demonstrate such relationships in ductile

materials when single crystals are not available for full analysis. (auth)—NSA.
16687

3.7.4, 3.7.3, 2.3.9, 6.3.10
Crystallites and Twinning in Cold-Rolled Nickel. A. P. Young. Battelle Memorial Inst. J. Applied Phys., **29,** No. 7, 1127 (1958) July.

Electron micrograph is shown of section prepared from sheet of electrolytic nickel which had been cold reduced to 1 mil and was subsequently cold reduced to 0.5 mil. Crystallite range, 0.1-0.8 micron, is within range estimated from x-ray studies. Parallel-sided bands in some crystallites indicate that deformation twinning also occurs in cold-worked nickel.—INCO.
16680

3.7.4, 3.5.3
Effect of Grain Size on the Resistance of Steels to Cavitation Erosion. (In Russian.) I. N. Bogachev and R. I. Mints. Metalloved. I Obraotka Metallov, No. 8, 26-29 (1958) Aug. Translation available from Henry Brutcher, Technical Translations, P. O. Box 157, Altadena, Calif.

Experimental study of effect of grain size and nature of grain boundaries on cavitation resistance of steel. Relationship between grain size and resistance of single-phase (austenitic, ferritic) steel; mechanism of cavitation destruction. Cavitation erosion in steels with duplex structures as function of grain size, component making up the network and cooling rate. Effect of brittleness or toughness of steel; mechanism of cavitational failure. 7 figures.—HB.
16750

3.8 Miscellaneous Principles

3.8.2, 3.8.4
Electrochemistry and Corrosion. (Concluded.) (In French.) M. Pourbaix. Corrosion et Anticorrosion, **5,** 286-293 (1957) October.

Corrosion behavior of iron in bicarbonate of sodium solutions of varying pH; of 18-8 stainless steel in acetic and acetate solutions with and without sodium chloride; influence of chlorides and phosphates on corrosion of iron and common steel; conditions required for passivation; practical application of theories deduced from observations (e.g., corrosion protection of reinforcement iron in concrete towers for overhead electric lines); methods of calculating corrosion rate of metals and alloys used in nuclear reactors, boilers, autoclaves, etc., at high temperatures and pressures. 42 references.—BTR.
16275

3.8.2, 6.2.2
Lessons on Electrochemical Corrosion. Pt. I. (In French.) M. Pourbaix. Centre Belge d'Etude de la Corrosion, Rapport Technique, No. 57, 1-19 (1957) Nov.

A study of corrosion from the economical and technical viewpoint. Reaction of iron in different aqueous solutions, in a sodium hydroxide solution, and in nitric acid iron used as anode or cathode. Effect of electric currents. Application of electrochemical thermodynamics to iron, zinc and manganese. 7 plates.—BTR.
16242

3.8.3, 6.2.2, 6.6.5
Corrosion of Iron in general and of Concrete Reinforcement in Particular. (In French.) M. Berthier. Revue de Materiaux, No. 511, 101-105 (1958) April.

Corrosion viewed as risk to be dealt with before occurrence; theory of passivation of iron; passivation techniques, use of low-solubility salts such as phosphates and fluorides. 3 references.—MR.
16466

3.8.3
Passivity of Metals. (In German.) H. Gerischer. Angewandte Chemie, **70,** No. 10, 285-298 (1958) May 21.

Cause of passivity of metals. Oxide layers are often extremely thin, down to monoatomic chemisorption layers of oxygen. Amperage/voltage diagrams to indicate passivation. Special problems of passivity.—BTR.
16512

3.8.4, 2.3.9., 3.4.9, 6.4.2
Hydrogen and Oxygen Isotopes Applied to the Study of Water-Metal Reactions. Exchange of D_2O^{18} with Alpha Alumina Monohydrate. R. B. Bernstein. Argonne National Lab. U. S. Atomic Energy Commission Pubn., ANL-5889, August 1958, 15 pp. Available from Office of Technical Services, Washington 25, D. C.

Isotopes of hydrogen and oxygen may be useful in elucidating the mechanism of aqueous corrosion reactions, in which an important step may be diffusion of protons and/or hydroxyl (or oxide) ions through a thin protective film. The technique of isotope exchange and the kinetic isotope effect both appear applicable. For the reaction between water and aluminum, the product (above 90 C) is α-alumina monohydrate (α-AlOOH). The exchange of D_2O^{18} with α-alumina monohydrate (submicron crystallite size) was examined from 100 to 230 C. The rate of deuterium-hydrogen exchange was appreciable; O^{18} exchange was slow. The O^{18} content of the separate phases suggested that only half the oxygen atoms in α-alumina monohydrate are exchangeable. Results were interpreted on the basis of a slow step involving independent diffusion of protons and oxygen carrier ions. The activation energy for the proton diffusion coefficient was approximately 12 kcal. The isotope exchange technique was applied to the reaction between water and aluminum at 100 C. Aluminum (type 1100) sheets reacted with water to the "protective film" stage, then with D_2O. The deuterium content of the film increased, but the net exchange (corrected for deuterium uptake) was only slight. Impurities (iron and silicon) in the aluminum may enter into the α-alumina monohydrate lattice and reduce proton mobility. Further corrosion-exchange studies with pure aluminum are needed to decide whether or not there exists a relationship between proton lability and corrosion rate. The deuterium isotope effect on the rate of aqueous corrosion reactions should be useful in assessing the importance of proton mobility in the mechanism. (auth)—NSA.
16745

3.8.4, 4.3.5, 6.3.10
Kinetics of the High-Temperature Heterogeneous Reaction of Chlorine and Nickel Between 1200 and 1700 K. John D. McKinley, Jr. and Kurt E. Shuler. National Bureau of Standards. J. Chem. Phys., **28,** 1207-1212 (1958) June.

The kinetics of the reaction of gaseous chlorine with metallic nickel has been investigated in a constant pressure flow system in the temperature range from 1200 to 1700 K, and at chlorine pressures between 0.08 and 0.4 mm mercury.

Nickel chloride produced in the overall reaction, $Ni_{(s)} + Cl_{2(g)} \rightarrow NiCl_{2(g)}$, is highly volatile at these temperatures, and the reaction thus takes place on the exposed metal surface. The process whereby nickel is removed from the surface is first order in chlorine pressure, very rapid with a collision efficiency between 0.5 and 0.2, and is temperature independent, i.e., $E_{act} < 2$ kcal. The rate constnt for the removal of nickel is found to be 1.85×10^5 cm sec^{-1} the units corresponding to moles of nickel per cm^2 of surface per unit density (M/cm^3) of chlorine. An experimental technique employing time lapse photography is described which is particularly well suited to the study of the kinetics of high temperature surface reactions with volatile reaction products. (auth)—NSA.
16559

3.8.4, 6.3.20
Variations in Length and Density Accompanying the Adsorption of Hydrogen by Zirconium. (In French.) Lucien Espagno, Pierre Azou and Paul Bastien. Compt. rend, **247,** 83-86 (1958) July 7.

The adsorption of hydrogen by zirconium causes linear variation in the length and density of samples of the metal. These variations are sufficiently sharp and reproducible to be used for the determination of the gas content of zirconum. (auth)—NSA.
16480

3.8.4, 6.4.2
Selective Oxidation of Aluminum from an Aluminum-Iron Alloy. Richard E. Grace and Alan U. Seybolt. J. Electrochem. Soc., **105,** No. 10, 582-585 (1958).

The selective oxidation of aluminum from a 4.8 wt% aluminum-iron alloy was studied with a microbalance at temperatures of 700-900 C. The oxidizing gas was damp hydrogen with dewpoints ranging from -55 to $0°$ C. The oxidation product was identified by electron diffraction to be the crystalline spinel. γ-aluminum oxide. At 800 C the parabolic oxidation constant was approximately proportional to the $\frac{1}{4}$th power of the water-hydrogen gas ratio, and the experimental activation energy for the over-all oxidation reaction with $0°$ C dewpoint hydrogen gas was 72 kcal/mole.
16532

3.8.4, 6.3.20
Development of a Cubic Oxide Protective Film on Zirconium. J. R. Johnson. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., ORNL-2029, Feb. 21, 1956 (Declassified March 2, 1957), 10 pp. Available from Office of Technical Services, Washington, D. C.

The cubic form of zirconium dioxide has been formed by the air-oxidation of binary zirconium alloys containing niobium, yttrium, or cerium in the temperature range 300 to 70 C.—NSA.
16220

3.8.4, 2.3.6
Oxidation Patterns on Metal Surfaces. (In German.) S. Yamaguchi. Werkstoffe u. Korrosion, **8,** 733-735 (1957) Dec.

Study of oxide film structures on metal surfaces subjected to oxidation, using electron-microscopic techniques. Oxide films can give indications regarding lattice type of base metal and alloy. Supporting data are given on oxide films formed on nickel, iron-chromium, nickel-iron and nickel-chromium-iron alloys.—INCO.
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3.8.4, 3.7.2, 6.3.6

The Effect of Beryllium on the Form of the Internal-Oxidation Precipitates on Heating Copper-Chromium Alloys in Air. (In French.) Donald Whitwham, Michel Scheidecker and Jean Hérenguel. Compt. rend., **245**, No. 18, 1540-1542 (1957) October 28.

During a study of the kinetics of subcutaneous oxidation of copper-chromium 0.6-0.9% alloys, a complete change of structure of this internal-oxidation zone was observed when 0.15% beryllium was added to the alloy: the rate of oxidation is retarded; precipitation of the oxide occurs at certain grain boundaries; but above all the periodic edging roughly parallel to the metal/oxide interface is observed. This edging is broken and not related to the texture of the base. Microhardness measurements of annealed and quenched specimens showed a difference between the core and the zone of internal oxidation. —MA.   16353

3.8.4, 3.2.3

Anomalies in the Growth of Anodic Oxide Films on Rough Surfaces. L. Young. Acta Metallurgica, **5**, No. 12, 711-716 (1957) Dec.

During growth of anodic oxide films, surface irregularities of scale of the thickness of the oxide film are believed to be flattened. Original inner layers of oxide (new layers are formed on outside) are constrained to cover progressively smaller area. Resultant compressive stresses produce failure if original metal surface is rough. With such surfaces progressively less charge is required to form oxide to a given potential at a fixed current density. Alternating current impedance measurements were made to test this theory. Capacity is smaller and dielectric losses are increased. Capacity increases with time after stopping current. With removal of bubbles, series equivalent capacitance should increase to value greater than normal since thinner oxide is exposed, and leakage is greater than normal; this was not observed. New theory is proposed. Test were conducted on chemically polished and buffed tantalum sheet specimens; oxide films were formed with automatic electronic control from 0.2 normal sulfuric acid solution. Graphs.—INCO.   16343

4. CORROSIVE ENVIRONMENTS

4.4 Chemicals, Organic

4.4.10, 5.8.2, 8.9.2

Study of Corrosion Inhibitors and Antioxidants for Glycol-Ethers. C. B. Jordon. Aberdeen Proving Ground, U. S. Army Ordnance Corps. May, 1957, 29 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 131398).

Combinations of chemicals were found which satisfactorily inhibit the corrosive activity of glycol-ethers, solvents which are widely used as components of automotive hydraulic brake fluids. Fluids containing three glycol-ethers of different basic chemical structure were subjected to corrosion tests. The brake fluid with the best standby storage results contained B, B^1-methoxy-methoxy-ethanol (MME) as its main solvent ingredient. Although combinations of chemicals inhibited specific glycol-ethers, no specific class could be found which gave consistently good results
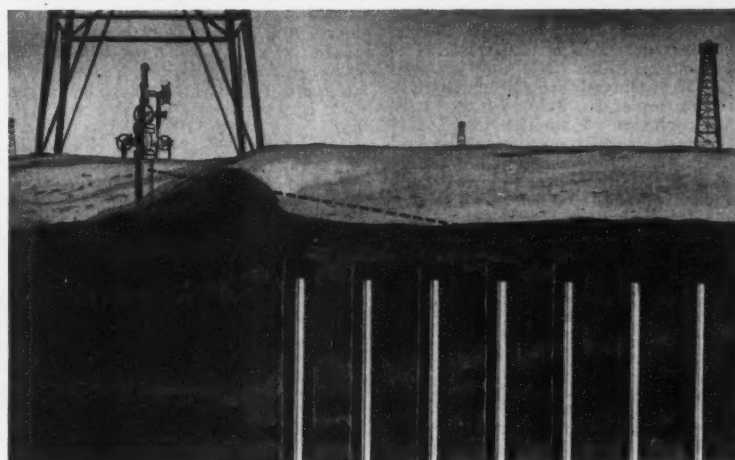
with the glycol-ethers in general. Except for MME, attack on all metals by glycol-ethers was found to be greater than attack by alcohols or glycols.— OTS.   15909

4.4.7, 3.6.5

Electrochemical Nature of Corrosion of Metals in Lubrication Oils. (In Russian.) I. A. Ptashinskii and R. I. Guseva. Khim. i Tekhnol., Topliv, 3, No. 5, 65-68 (1958) May.

Voltages changes generated between copper and lead electrodes in a bath of lubricating oil indicate that corrosion of metals in oils is an electrochemical process. The two electrode plates separated by a gap of 1 mm were partly immersed in an oil bath in a thermostat at 140 C for 3 hours or more while passing air therethrough at the rate of 0.05 liters/min. One series of experiments was conducted with ordinary oils and the second with the same oils plus 5% of TsIATIM-339 additive (composition not given). With plain oils, the voltage rises in 3 hours to a maximum and then decreases during the next 11 hours. The first period reflects chiefly progressive oxidation of the oil and the second, after the maximum, the formation and accumulation of the lead salt. The voltage curve for oils with the additive shows a sharp drop within 1-1.5 hrs, apparently because the additive has inhibiting effect on oxidation. Thereafter the action of the additive is manifested by gradual rise of voltage over 4-5 hours and formation of a colored protective film on the electrode surface. The results were confirmed by polarographic determination of lead in the oil.   16731

The Effect of Sulfur Compounds on the Service Qualities of Hydrocarbon Fuels. Ya. B. Chertkov and V. N. Zrelov. J. Applied Chem. USSR (Zhur. Priklad. Khimii), **31**, No. 10, 1384-1389 (1958).

The group composition of the sulfur compounds of fuels boiling in the range of naphthakerosine fractions is determined in relation to the thermal stability of the sulfur compounds and the nature of their action on the corrosion activity and deposit-forming tendency of the fuels. 4 tables, 19 references.—ATS. 16468

4.5 Soil

4.5.1, 5.2.1, 6.2.1, 5.3.2

Evaluation of Soil Corrosion at Hanford Atomic Products Operation (Summary Report: Underground Pipeline and Structure Corrosion Study Program). R. T. JASKE. Hanford Atomic Products Operation. U. S. Atomic Energy Comm. Pubn., HW-33911, April 15, 1955 (Changed from Official Use Only November 26, 1956), 61 pp.

The corrosion of stainless steel, cast iron and galvanized steel pipes by soil conditions is summarized. The use of cathodic protection for stainless steel pipe is recommended. Other similar recommendations are offered.—NSA. 13644

4.5.1, 3.2.2

Underground Corrosion. Pt. I. Corrosion Mechanism of Metals in Soil. Corrosion Technology, **5**, 5-9 (1958) Jan.

Bureau of Standards report on corrosion mechanism of metals in soil free of stray currents. Graphitization may decrease or accelerate the normal rate of corrosion; physical or chemical properties of the soil control the character of corrosion; pitting factors are roughly proportional to the ratio of the uncorroded areas. In well-aerated soils the rate of pitting, although initially great, falls off rapidly with time, whereas, in poorly-aerated soils, the initial rate scarcely falls off with time. Low-alloy steels have a greater pitting rate than the plain steel; however, as the exposure increases, the rate of pitting of the alloy steels diminishes more rapidly than the plain steel. High-alloy steels, especially chromium and nickel, decrease the weight loss through the entire range. —MR. 16447

4.5.3

Cathodic Protection for Earth-Buried Pipelines and Other Metal Structures. J. H. Bird and A. Z. Dimitroff. U. S. Interior Dept., Bureau Mines Information Circular No. 7827, April 1958, 27 pp.

General principles of this method of inhibiting corrosion are explained in terms of relationship between soil resistivity, protective grounding and cathodic protection. Galvanic anodes, electrolytic anodes, soil resistivity measurements, stray currents, bonding and protective grounding are discussed. Illustrations are presented of the cathodic protection installations of El Paso Natural Gas Co. Use of cathodic protection in mining industry is urged.— INCO. 16456

4.5.3, 7.2

Localization of Corrosion Damage in Underground Pipes. (In German.) HEINRICH KLAS AND GERHARD HEIM. Gas- und Wasserfach, **98**, No. 44, 1103-1106 (1957) Oct. 31.

Measurements of the specific ground resistance at various depths according to the Wenner-process, whereby the ground conductivity, the dispersion rate of sediments, the conditions of precipitation and the permeability of the ground for air and water are analyzed.—BTR. 15315

4.6 Water and Steam

4.6.2, 3.5.9, 7.6.4, 6.2.3, 6.2.4

Oxidation of Superheater Materials by High-Temperature Steam. J. Hoke and F. Eberle. Paper before Am. Soc. Mechanical Engrs., Annual Mtg., New York, December 1-6, 1957. ASME Paper No. 57-A-175, 1957, 10 pp.; Abst: Combustion, **29**, No. 6, 50 (1957) Dec.

Results of exposure of six low and medium-alloy materials at various temperature levels ranging from 950-1250 F for 7323 hr during operation of an experimental super-heater indicate that there is a narrow temperature range over which oxidation begins to increase rapidly. This transition temperature is approximately 1050 F for carbon steel and 1100-1150 F for low-alloy steels. Addition of up to 5 chromium does not add materially to long-time oxidation resistance of low-alloy steel, but a chromium content of 9% markedly increases temperature at which oxidation becomes serious.—INCO. 16185

4.6.11, 7.4.2, 6.3.6, 6.4.2.

Sea Water Corrosion of Various Materials Tested in Seven 20-Tube Model Condensers. J. L. Basil and J. S. Whelan. Naval Research Lab. U. S. Naval Eng. Exper. Station, E.E.S. Rept. No. 910027A, (NS-643-078), March 21, 1958, 55 pp.

Seven 20-tube model condensers were tested at Harbor Island for corrosion and erosion resistance by pumping natural sea water through tubes at 10 ft/sec. One was an all-aluminum condenser. Others had 70-30 and 90-10 copper-nickel tubes with water boxes and tube sheets of various alloys (Monel, aluminum-bronze, 90-10 and 70-30 copper-nickel). Report describes condition of units after destructive examination. Number of conclusions are reached regarding relative performance of various materials, role of minor elements (iron and aluminum) on performance of copper-nickel tubes, and other factors including water box design, plastic tube inserts, galvanic effects and duplexing of tubes. Present tests confirm previous conclusion that iron-bearing 90-10 copper-nickel alloy is satisfactory alternate to iron-bearing 70-30 copper-nickel. All new condensers in surface vessels are tubed with 90-10. Since performance of 90-10 closely approaches, but does not quite equal, performance of 70-30 copper-nickel, 70-30 will continue to be specified for critical applications such as submarines. Use of 90-10 copper-nickel tube sheets and water boxes appears suitable for condensers with 90-10 tubes. Aluminum bronzes are not recommended unless there is critical shortage of nickel. Use of dual gage copper-nickel tubes is not recommended. Stainless steel/copper-nickel duplex tubes are satisfactory for use under special circumstances, e.g., to resist sea water on one side and acid condensates in closed-cycle systems on other side. 3S aluminum tubes with 72S aluminum cladding had useful life from corrosion standpoint; service trial

4.7 Molten Metals and Fused Compounds

4.7

Compatibility of Metals with Liquid Fluorine at High Pressures and Flow Velocities. Harold W. Schmidt. Lewis Flight Propulsion Lab. U. S. National Advisory Committee for Aeronautics, Research Memo E58D11, July 15, 1958, 16 pp.

Nickel, stainless steel, brass and aluminum were evaluated for compatibility with liquid fluorine at flow velocities up to approximately 400 ft/sec and pressures up to 1500 lb/sq in. gage. Configurations were varied to produce severe turbulence and impact effects. Two rotating-vane flowmeters were also tested. None of the metals exhibited any measurable physical or chemical changes. In a run made with Teflon, fluorine reacted violently. (auth).—NSA 16661

4.7, 3.8.4

Corrosion Mechanism of the Metals in Fused Chlorides. (In Russian.) N. D. Tomashov and N. I. Tugarinov. J. Applied Chem., USSR (Zhur. Priklad. Khim.), **30**, No. 11, 1619-1625 (1957) Nov.

A scheme of metal corrosion in fused salts could be represented in the following way; anodic process: discharge of metal ions into melt under the effect of salt anions, flowing of electrons from anode region to the cathode region, and the cathodic process: assimilation of electrons by depolarizer (oxygen, water, carbon dioxide, Ca++ and others).—BTR. 16392

4.7, 3.5.4, 6.2.5

Dissolution and Distribution by Liquid Sodium of Activated Type 347 Stainless Steel. A. M. Saul. North American Aviation, Inc. U. S. Atomic Energy Commission Pubn., TID-10021, March 15, 1954 (Declassified March 19, 1957), 26 pp. Available from Office of Technical Services, Washington, D. C.

The distribution by sodium of the radioactive elements of Type 347 stainless steel was studied under dynamic conditions using convection-diffusion capsules operating between 300 and 700 C. The nuclides identified as depositing on the initially inactive walls of these capsules are Ta^{182}, Fe^{59}, Co^{60}, Cr^{51} and Mn^{54}. Deposition of these activities does not seem to be a function of capsule wall temperature alone. It was found that the presence of oxygen greatly accelerate the transfer of activity. (auth).—NSA. 16341

5. PREVENTIVE MEASURES

5.2 Cathodic Protection

5.2.2, 1.2.2, 8.9.5

Reducing Cathodic Protection Costs in Tankers. L. R. Page. Corrosion Technology, **5**, No. 8, 257-259 (1958).

The author describes developments in cathodic protection designed to reduce costs and increase efficiency. Finned magnesium anodes have been used with success. High purity zinc anodes are considered the most effective for use on painted ships' hulls as their driving

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potential is lower than that of magnesium and so there is less tendency for the paint to be stripped. 5 illustrations.—ZDA.   16612

5.2.2, 5.4.5, 8.9.5
Cathodic Protection in Relation to Ships' Bottom Paints. H. W. Van Der Hoeven. J. Oil Col. Chem. Assoc., **40**, No. 8, 667-683 (1957).

Cathodic protection of ships may give rise to deterioration of the paint film; especially in the vicinity of the anodes. This deterioration may be due to the anode design, to the properties of the paint, or to both. The performance of a number of ships' bottom paint systems when used in conjunction with cathodic protection has been examined. Results of exposure tests with cathodically protected painted-steel panels in Amsterdam harbour and near the Hook of Holland are discussed. Furthermore, some results are given of tests with anodes designed to minimize damage to the paint and to supply an increasing amount of current on continuing exposure. These anodes make it possible to keep pace with the increase in current delivery necessitated by the gradual breakdown of the paint film by mechanical damage during its life.—RPI.   16391

5.2.3, 8.8.1
Cathodic Protection with Impressed Currents for Salt-Manufacturing Plants. Y. Sakae and M. Suzuki. Corrosion Engineering (Japan), **7**, No. 1, 31.35 (1958) Jan.

Results of a study of a salt-manufacturing plant's cathodic protection using impressed currents with insoluble anodes:

1. Cathodic protection with impressed currents is economically and technically superior to the galvanic anodes system.

2. Tests carried on insoluble anodes material showed the superiority of the magnetite anode (in high concentration salt-water) and the fair behavior of the high silicon cast iron anode.

3. In applying cathodic protection to salt-manufacturing plant, (a) the protective current density should be kept between 0.5-1.0 mA/cm² and (b) the necessary voltage between 2.5-4V. With high temperature conditions, however, severe depolarizing action requires larger protective current densities.—JSPS. 16653

5.2.3, 5.4.5, 8.9.5
Cathodic Protection of Shipping. D. S. Tulloch. Corrosion Prevention and Control, **4**, No. 6, 51-52 (1957) June.

When ships are painted in a shipyear, "holidays" in the painted surface are almost inevitable. On the submerged parts, these may become sites of electrolytic corrosion. Such corrosion and also that due to bimetallic couples, may be suppressed by cathodic protection; for a reasonably well painted hull, the current density should be about 2½ milliamps per sq ft of the total immersed steel. For the cargo-ballast tanks of oil carriers on which no really effective paint coating can be applied, the cathodic protection has to suppress corrosion by itself and the current should be of the order of 10 milliamps per sq ft.—RPI. 16400

5.2.3, 3.5.8, 4.6.11, 6.2.3
Corrosion-Fatigue of Mild Steel in Sea Water. Pt. I. The Influence of Cathodic Protection on the Corrosion-Fatigue. Y. Minami and H. Takada. Trans. Shipbuilding Assoc. Japan, No. 103, 165-170 (1958) May.

Reversed bending fatigue tests in sea water under the impressed current cathodic protection were carried out. The lower the electrochemical potential the higher the fatigue limit; in spite of a large quantity of absorbed hydrogen, no deterioration of the fatigue strength was observed. It is supposed that the distortion of the lattice structure produced by the absorbed hydrogen is favorable to the fatigue. Relations among potential, cathodic current and applied stress were also considered.—JSPS. 16547

5.3 Metallic Coatings

5.3.4
Studies on Electroless Nickel Plating. Clara H. de Minjer and Abner Brenner. Plating, **44**, No. 12, 1297-1305 (1957).

The results of laboratory investigations on eight electroless plating solutions are described. The rate of deposition increased with the amount of organic acid to a maximum and then descreased. Of more than 10 acids examined, lactic gave the highest rate followed by hydroxy acetic acid. Other factors studied included precipitate formation in the processing solution, the effects of copper and iron on operation, the reactivation of spent baths, the effect of inhibitors and other substances on nickel deposition rate and the comparative outdoor-exposure resistance of electroless nickel and electrodeposited nickel and nickel alloy coatings both containing 8-10% phosphorus. These alloys gave superior protection to the nickel plated coatings and

electroless deposits from acid baths had better corrosion-resistance than those from alkaline solutions. 14 references.—MA.   16145

5.3.4
The Basic Principles of Acid Copper-Plating and the Cupatier Process. W. Strauss and E. Roth. Metalloberfäche, 11, No. 9, 281-285 (1957).

The basic principles of bright-plating copper from acid baths on iron are discussed, with particular reference to the "Cupatier" process, in which the addition of small amounts of substances (unspecified) enables an electrolyte containing cupric sulfate 200-250 and sulfuric acid 40-70 g/l to be operated at 18-25 C and more than 8 amp/dm². Recommended procedures are noted for the direct plating of cast iron, hard steel, copper-base alloys and zinc die-castings. The properties of the coatings are described; these include: greater hardness, finer grain-size and better adhesion than is obtained with normal processes and, therefore, enhanced resistance to wear, cracking, peeling or deformation and corrosion.—MA.   16282

5.3.4, 4.4.2, 3.6.8
Effect of Naphthalene Sulphonic Acids on the Process of Nickel Electroplating. A. V. Pamfilov and O. E. Panchuk. Ukrain. Khim. Zhur., 23, 391-396 (1957).

Describes investigation of effect of number of naphthalene sulphonic acids on magnitude of cathode polarization during nickel electrodeposition at 25, 40 and 55 C in range of current densities of 0.1-2 amp/dm². Introduction of these acids is shown to have little effect on magnitude of cathode polarization, but some depolarization is occasionally observed. Explanation of results obtained is proposed, based on following phenomena: reduction of sulphonic acids, formation of nickel sulfide and reduction of the latter. Graphs.—INCO.   16247

5.3.4
Hot-Dip Aluminum Coating of Steel Wire. Masayoshi Tagaya and Shigeteru Isa. Technol. Repts. Osaka Univ., 7, No. 246, 133-140 (1957); Chem. Abstracts, 52, No. 10, 8009 (1958) May 25.

After fluxing with gaseous ammonium chloride, saturated aqueous solution of zinc chloride and ammonium chloride, or molten salts such as zinc chloride with 10% LiCl₂, the steel wire is immersed for 1-2 sec. in aluminum at 720-770 C. Long immersion time and high temperature of the aluminum increases the thickness of the iron-aluminum alloy layer and results in lowered tensile strength and increased elongation of the wire. In solutions of pH 4-8 at room temperature, aluminum-coated steel is more corrosion-resistant than galvanized steel.—ALL.   16415

5.3.4, 6.3.14
Corrosion Resistance of Tin Alloy Electrodeposits. Frederick A. Lowenheim. Proc. Am. Electroplater's Soc., 44, 42-46; Disc., 160 (1957).

Advantages and limitations of using tin and tin alloys for corrosion prevention. Compositions and results of exposure tests on tin and tin alloys for corrosion prevention. Compositions and results of exposure tests on tin-zinc, tin-cadmium, tin lead, tin-nickel and tin-copper alloys. Tin is good undercoat for zinc and cadmium in marine environment and can be used for undercoat of both organic and metallic coatings. Although tin-zinc alloy is not choice coating for protection of steel, it appears promising in contact with aluminum.

Superiority of bronze over copper as undercoat in nickel-chromium systems is shown. 35 references.—MR.   16227

5.3.4, 8.4.5
Electrokinetic Processes—Nuclear Aspects. Quarterly Progress Report for February 1-April 30, 1954. Vitro Corp. of America. U. S. Atomic Energy Commission Pubn., KLX-1721, May 15, 1954 (Declassified March 1, 1957), 23 pp. Available from Office of Technical Services, Washington, D. C.

The preparation of metallic coatings by electrophoretic deposition of metallic oxides and by subsequent reduction and sintering in purified hydrogen was studied. A technique was developed for the electrophoretic deposition of smooth, uniform coatings of silicon carbide, suitable for all metallic carbides. A procedure for the preparation of a ZrH₄-alcohol dispersion with good electrophoretic coating properties was studied, and the application of porcelain enamels by electrophoretic deposition was investigated in an effort to obtain thin uniform ceramic coatings on aluminum for corrosion protection. Since a monitoring device was necessary for the control of electrophoretic plating, tests were made with two types of automatically recording balances, a strain gage unit and an electromagnetic unit, to weigh continuously the material plated per unit time. A process was developed for the preparation of electrophoretic coating dispersion by a precipitation process. The preparation of uranium dioxide-alcohol dispersion is described.—NSA.   16365

5.3.4, 6.2.4
High-Temperature Carburizing Takes Half the Time. P. M. Unterweiser. Iron Age, 181, No. 21, 123-125 (1958) May 22.

Standard low-alloy steels such as 4620, 8620 and 9310 can be advantageously carburized at temperatures above the conventional carburizing temperature range (1700-1725 F). A case depth normally achieved in 12 hours can be attained in six hours when carburizing temperature is increased to only 1800 F. Graph shows carburizing rates for Russian titanium-modified low-alloy steel 18KhGT. Tables, Photomicrograph. (auth)—INCO.   16704

5.3.4, 6.2.2
Nitriding of High-Strength Magnesium-Treated Cast Iron. Yu. M. Lakhtin and D. S. Pinchuk. Metalloved. I Obrabotka Metallov, No. 7, 39-42 (1958) July. Translation available from Henry Brutcher, Technical Translations, P. O. Box 157, Altadena, Calif.

Study of rate of formation and nature of phases present in nitrided cases on magnesium-treated cast irons. Properties of case as function of nitriding temperature and time. Hardness variation in depth of case. Micrographic analysis of nitrided case. Distribution of nitrogen in case. Similarity in kinetics of formation of nitrided case on cast iron and on steel. 6 Figures.—HB.   16576

5.3.4, 6.4.2
Surface Treatment and Finishing of Light Metals. Pt. XII-D. Plating on Aluminum—The Vogt Process. S. Wernick and R. Pinner. Metal Finishing, 55, No. 4, 68-71 (1957) April.

Description of Vogt process of plating aluminum articles in finishing of holloware. Vogt process is characterized by application of an electrodeposited zinc film which can be produced with certainty irrespective of composition or construction of aluminum components.

Zinc deposit is uniform but because it is too thin to resist chemical attack when subjected to normal nickel plating solution, a thin deposit of brass is superimposed on it. After final plating with nickel and before chromium plating, components are subjected to heat treatment. All types of aluminum alloy may be nickel-chromium plated except those which contain magnesium in excess of 3%. Tables, diagram.—INCO.   16383

5.6 Packaging

5.6.1
A Survey of Corrosion in Packaging. D. V. Weatherly. Corrosion Prevention and Control, 5, No. 2, 47-50, 74 (1958) Feb., ibid., No. 3, 59-61 (1958) March.

Reviews causes of corrosion in packaged articles and discusses various preventive measures. Humidity factor is dealt with. Semi-rigid barriers include cartons dipped in wax and so-called moldable wrap. Spray packaging employs various kinds of vinyl polymers; Cocoon and Texikoon are cited. An impermeable envelope, Dri-Clad, is made of sandwich of polyvinyl chloride, cotton cloth, and foil. Various types of temporary coatings which are removed with solvents or by stripping are described. Use of vapor phase inhibitors is considered. Various types of vapor phase inhibitors available and methods of determining their effectiveness within packages are discussed. Use of polythene packaging and treatment of paper for packaging are considered.—INCO.   15505

5.6.3, 3.3.4, 4.2.7
Protection Against Corrosion During Naval Transport in Tropical Climates. (In German.) HERMANN DETERMANN. *Werkstoffe u. Korrosion*, 8, 689-694 (1957) Nov.

Special observations were made during trial runs on steel products. Insufficient amounts of silica gel as drying medium may result in slight to severe corrosion depending on tightness of package. Bacteria favor corrosion and bananas can breed bacteria. Anticorrosive greases and wax help. Vapor phase inhibitor is a good anticorrosive. 7 references.—MR.   15230

6. MATERIALS OF CONSTRUCTION

6.2 Ferrous Metals and Alloys

6.2.1
How the 200 Series Compares with 18-8 Stainless Steel. G. A. Sands and M. B. Keady. Electro Metallurgical Co. Materials in Design Eng., 47, No. 4, 120-123 (1958) April.

Research, testing and use of 200 series steels have proved that they are for the most part every bit as good as the steels for which they were once considered alternates. It has been variously estimated that 75-90% of the uses of 18-8, types 301 and 302 can be completely served by types 201 and 202. Tensile properties of 200- and 300-series are comparable, although yield strengths and hardnesses of 200 series are somewhat higher. 200 series steels are comparable with corresponding 300 grades in atmospheric exposure and under oxidizing conditions. In virtually all instances, 200 series steels can be formed in the same manner and with the same equipment as 300 series. Cost of 200 series is less and availability is better. Photos, tables.—INCO.   15663

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6.2.2, 8.8.5

Roundup of Ductile Iron Technology.
D. Matter. Ohio Ferro Alloys Corp.
Modern Castings, **33**, No. 3, 24-27 (1958)
March.

Review of ductile iron technology
covers effect and control of graphite
form, matrix structures produced
through alloy control, ferritic nodular
iron, heat treatment of castings, chemical control, melting units, sulfur control,
gating and risering. Profile of ductile
iron properties covers its wear resistance, strength, ductility, castability, impact resistance, corrosion resistance and
pressure tightness. Typical stress-strain
curves are shown.—INCO.   16090

6.2.4

Coming: Better Thermenol Alloys.
W. J. Buehler and C. G. Dalrymple.
U. S. Naval Ordnance Lab. Metal Progress, **73**, No. 5, 78-81 (1958) May.

Iron-aluminum alloys with 3 to 4%
molybdenum have excellent oxidation
resistance and stress-rupture strength.
The alloys are useful for high-temperature applications with small additions
of zirconium and carbon to raise the
mechanical properties and inhibit grain
growth. The preparation and some
properties are discussed.—NSA. 15930

6.2.5

Stainless Steels for Corrosion Resistance. L. R. Honnaker. Chemical Engineering Progress, **54**, 79-82 (1958) Jan.

Causes, means of avoiding failures in
stainless steel equipment resulting from
pitting crevice corrosion, intergranular
corrosion, stress-corrosion cracking and
related phenomena where general corrosion is slight. 6 references.—MR.
15616

8.   INDUSTRIES

8.3 Groups 3

8.3.3, 6.4.2

Aluminium for the Dairy Industry.
J. C. Bailey. J. Soc. Dairy Technology,
11, No. 2, 50-57; disc., 57-58 (1958).

The use of aluminum in transport
tanks and rigid containers as well as in
the form of foil and collapsible tubes
for the canning and packaging of dairy
and food products is discussed. Bailey
lists uses of aluminum and its alloys in
dairy plant, transport, milking equipment, packaging and buildings. The
effect on aluminum in contact with detergents and with supply waters of varying compositions is reviewed. The various groups of wrought and cast
aluminum alloys and their fabrication

are briefly discussed. Developments in
cladding aluminum alloys with high-purity aluminum for corrosion-resistance
and in aluminized steel are mentioned.
The compatibility of aluminum with
stainless steel and plastics is referred
to and their potential uses in combination with each other. In the discussion,
the anodic treatment of aluminum is
considered.—MA.   15969

8.3.6, 5.2.2

Corrosion and Anti-Corrosive Protection in the Sugar Industry. B. Mantovani. Metallurgia Italiana, **49**, No. 9, 669-
672 (1957).

To investigate whether sacrificial
anodes could usefully be employed for
protecting iron surfaces in sugar plants
from corrosion, Mantovani made tests
with magnesium and zinc anodes
screwed to iron sheets immersed in 10-
50% sugar solution at 25, 40 and 85 C.
Magnesium gives somewhat better protection than zinc as judged by the
amount of iron going into solution, and
much better as judged by the amount of
reducing sugar formed, this being due
to control of the pH by the Mg^{2+} or Zn^{2+}
going into solution. These results are
promising. 15 references.—MA.   15880

8.5 Group 5

8.5.2

**Corrosion Prevention in the Bottling
Industry.** L. A. Johnson. Corrosion
Technology, **5**, No. 3, 81-83, 94 (1958)
March.

Factors causing corrosion in bottling
plant are presence of water and high
humidity in atmosphere, presence of dissimilar metals and action of detergents
on paint coatings. Proper design of
plant and equipment, use of corrosion-proof materials, selection of paints and
primers and use of impregnated wrapping tape are discussed. Mention is made
of control of mold growth.—INCO.
15679

8.5.4, 5.8.4, 3.3.4

**Performance Tests of Heavy Metal
Compounds as Marine Borer Inhibitors.**
T. ROE, JR., H. HOCHMAN AND E. R.
HOLDEN. Paper before Am. Soc. for
Testing Materials, 2nd Pacific Area Nat.
Mtg., Symp. on Wood for Marine Use
and Its Protection from Marine Organisms, Los Angeles, Sept. 17, 1956.
ASTM Special Tech. Pubn. No. 200,
29-32; disc. 33-34 (1957).

Performance tests of various oxides
and sulfides of the heavy metals, including nickel sulfide, indicate a relatively
short service life for wood impregnated
with these compounds. Service life, in
optimum cases was increased by 1-2
years over the 4 months for untreated
wood. Effectiveness of protection against
Teredo larvae of metals as insoluble
compounds in wood, in decreasing order,
was as follows: copper, silver, nickel,
lead, mercury and iron. Zinc and cadmium were practically ineffective. Effectiveness against Limnoria, in decreasing
order, of metals as insoluble compounds
in wood was as follows; copper, nickel
and mercury. Others were ineffective.
Effectiveness of metals, in decreasing
order, as soluble compounds in the biological testing procedure was as follows;
mercury, copper, cadmium, silver, zinc
and cobalt. Nickel, aluminum and lead
were ineffective. None of these compounds, however, showed an effectiveness approaching that of creosote. R. B.
Teel and F. L. LaQue (Inco) participated in the discussion.—INCO. 15111

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